Researches, Publications and Achievements

2007-2011

Department of

Macromolecular Science and Engineering

Kyoto Institute of Technology

Contents

Functional Polymer Design Laboratory

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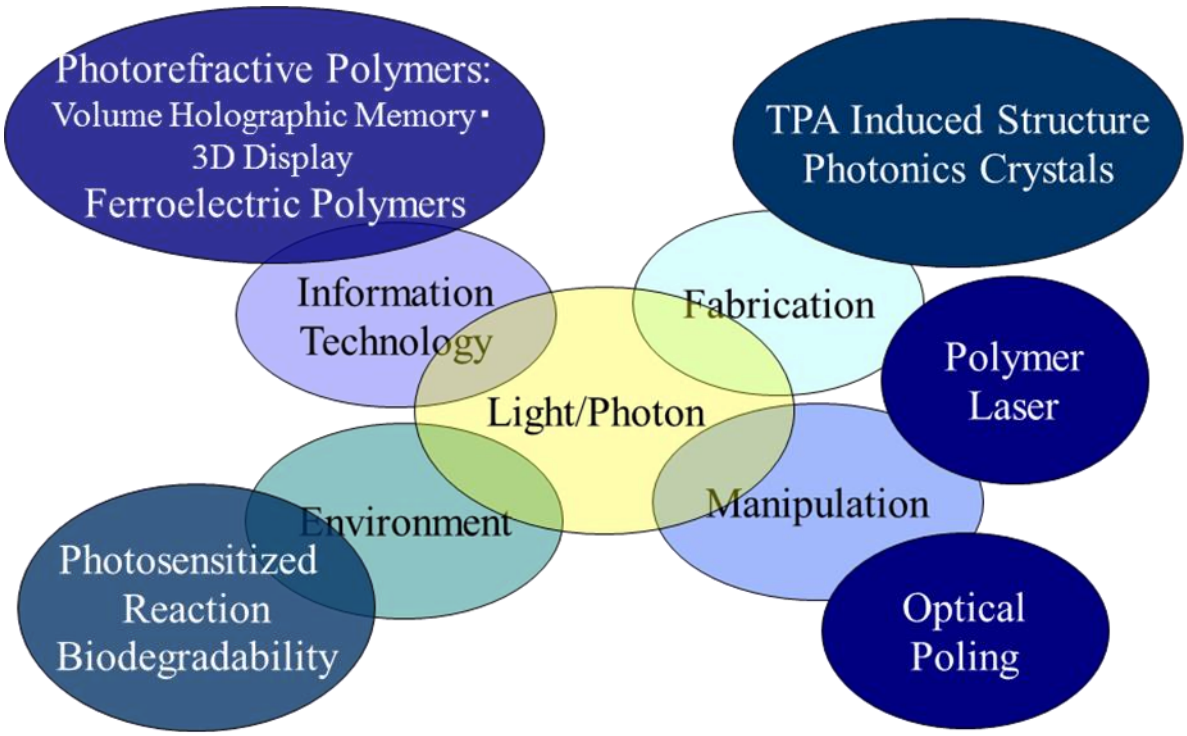
Kenji KINASHI, Dr., Assistant Prof.

I. Researches

Tsutsumi's laboratory focuses on the interaction between light, photon and matter. We have 5 main research themes as follows.



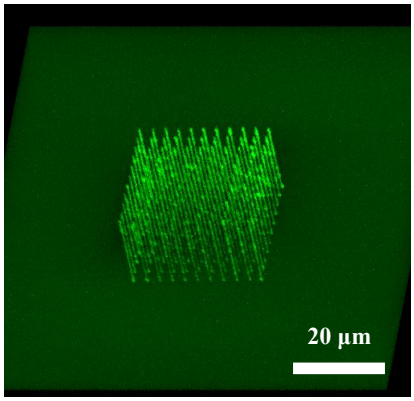
Individual Research Contents

1) For information technology, photorefractive (PR) polymers have been developed. PR polymers are the promising materials for the next generation three dimensional (3D) holographic display and volume holographic memory system. Photorefractive effects are based on the refractive indices modulation shifted to the interfered light pattern in the PR polymers possessing photoconductivity and 2nd order optical nonlinearity (NLO). Periodic space charge field created by the photo-generated charge carriers induces the Pockels effect through NLO chromophore in the PR polymers, and Pockels effect, nonlinear refractive index modulation, is induced by these periodic space charge fields. Dynamic holographic imaging can be produced using PR polymers. Our research objectives are the real-time 3 D holographic display with video-rate using PR polymers.

Reconstructed hologram image of coins using photorefractive polymer.

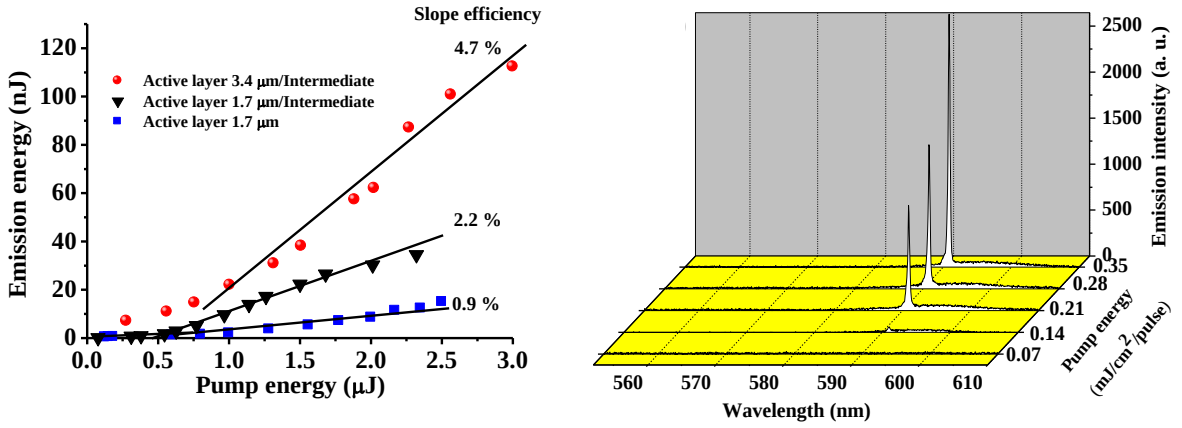
2) Related to the information technology, ferroelectric polymer devices are developing. Fast ferrolectric switching up to 100 kHz is achieved for poly(vinylidene trifluoroethylene) (P(VDF-TrFE) copolymer) thin film.

3) For fabrication of structures by light or photon, laser lithography based on two photons absorption (TPA) is used. Laser source is a femtosecond Ti-Sapphire laser. Micron scale and sub micron scale 3D structures can be fabricated in the samples using TPA under a microscope with a high NA object lens. Lithographic photopolymers is used to fabricate 2D or 3D structures. Silver micron structures can be fabricated using photo-reduction of silver ion by TPA technique. Fabrication of photonic crystals and light cloaking materials (metamaterials) using TPA are our current objective.



CLSM images of three dimensionally fabricated Ag structures.
Naoto Tsutsumi, Kazuya Nagata and Wataru Sakai, "Two-photon laser fabrication of three-dimensional silver microstructures with submicron scale linewidth", *Appl. Phys. A* **103**, 421–426 (2011).

4) For manipulation of light or photon, organic dye laser devices have been developed. Organic distributed feedback (DFB) and distributed Bragg reflection (DBR) lasers have been fabricated using an organic waveguide polymer. Low threshold down to nJ or pJ and high slope efficiency in the order of tens % are current objective.



Slope efficiency and threshold for polymer laser.
N. Tsutsumi and M. Shinobu, "All organic DFB Laser Enhanced by Intermediate High Refractive Index Polymer Layer", *Appl. Phys. B* **105(4)**, 839-845 (2011).

5) Related to the environment, photosensitized reaction and photosensitized biodegradability of polymers have been investigated using direct measurement of an electron spin resonance (ESR) spectroscopy and spin trapped method based on ESR spectroscopy. Radical species are assigned from ESR signals, from which the reaction mechanism can be modeled. Simulation technique also supports the evaluation of reaction mechanism.

II. Publications and Achievements

(a) Original papers

2007

1) Naoto Tsutsumi and Arata Fujihara, "Self-assembled Spontaneous Structures Induced by a Pulsed Laser on a Surface of Azobenzene Polymer Film", *J. Appl. Phys.* **101**, 033110 (5 pages) (2007).
2) Naoto Tsutsumi, Shinya Yoda and Wataru Sakai, "Infrared spectra and ferroelectricity of ultrathin films of vinylidene fluoride and trifluoroethylene copolymer", *Polym. Int'l.* **56**, 1254-1260 (2007).
3) Minoru Nagata, Ryosuke Sugiura, Wataru Sakai, and Naoto Tsutsumi,"Synthesis and Characterization of Biodegradable Network Poly(ethylene glycol) Films with Elastomeric Properties", *J. Appl. Polym. Sci.* **106 (5)** 2885-2891 (2007).
4) Naoto Tsutsumi and Masayuki Otsuji,"Crystalline Structures, Surface Morphology and Ferroelectric Response in Ultra-thin Film of Vinylidene Fluoride and Trifluoroethylene Copolymer", *J. Appl. Phys.* **102**, 104101 (4 pages) (2007).

2008

5) N. Tsutsumi, Y. Kono, M. Oya, W. Sakai and M. Nagata, "Recent development of biodegradable network polyesters obtained from renewable natural resources", *Clean* **36(8)**, 682-686 (2008).
6) N. Tsutsumi, A. Fujihara, K. Nagata, "Fabrication of laser induced periodic surface structure for geometrical engineering", *Thin Solid Films* **517**, 1487-1492 (2008).
7) N. Tsutusmi and Y. Ikegami, "Second-oeder optical nonlinearities from $\chi^{(2)}$ gratings induced by holographic all-optical poling", *Optics Commun.* **281**, 5905-5909 (2008).
8) N. Tsutsumi and H. Kasaba, "Effect of molecular weight of poly(N-vinyl carbazole) on photorefractive performances", *J. Appl. Phys.* **104**, 073102 (2008).
9) M. Nagata, T. Tanabe, W. Sakai, and N. Tsutsumi, "Preparation and properties of biodegradable network poly(ester-carbonate) elastomers", *Polymer* **49**, 1506-1511 (2008).
10) N. Tsutsumi, Y. Ito, and W. Sakai, "Effect of sensitizer on photorefractive nonlinear optics in poly(N-vinylcarbazole) based polymer composites", *Chem. Phys.* **344**, 189-194 (2008).
11) N. Tsutsumi and M. Takeuchi, "All-plastic organic dye laser with distributed feedback resonator structure", *Thin Solid Films* **516**, 2783-2787 (2008).
12) N. Tsutsumi and M. Takeuchi, "Ti-sapphire femtosecond pulse pumped laser emission from all-plastic organic waveguide with distributed feedback resonator", *Optics Commun.* **281**, 2179-2183 (2008).

2009

13) Naoto Tsutsumi and Takashi Ishibashi, "Organic Dye Lasers with Distributed Bragg Reflector Grating and Distributed Feedback Resonator", *Optics Express* **17 (24)**, 21698-21703 (2009).
14) Naoto Tsutsumi and Wataru Miyazaki, "Photorefractive Performance of Polycarbazoylethylacrylate Composites with Photoconductive Plasticizer", *J. Appl. Phys.* **106**, 083113 (2009).
15) Naoto Tsutsumi, Tomohiro Yamaoka, "Ferroelectric Properties of Ultrathin Films of Nylon 11", *Thin Solid Films* **518**, 814-818 (2009).
16) T. Yamao, T. Inoue, Y. Okuda, T. Ishibashi, S. Hotta and N. Tsutsumi, "Gain-narrowed emissions from oligomer crystals assisted by interference exposure", *Synth. Met.* **159**, 889-892 (2009).

2011

17) N. Tsutsumi and M. Shinobu, "All Organic DFB Laser Enhanced by Intermediate High Refractive Index Polymer Layer", *Appl. Phys. B* **105(4)**, 839-845 (2011).
18) Y. Makino, T. Hinode, A. Okada, T. Yamao, N. Tsutsumi, S. Hotta, "Spectrally-Narrowed Emissions from a Layered Organic Transistor Equipped with a Diffraction Grating", *Phys. Procedia* **14**, 177–181 (2011).
19) N. Tsutsumi, K. Kinashi, and W. Sakai, "Strategy for high performance photorefractive polymer composites", (Polymer Photonics, and Novel Optical Technologies edited by Y. Kawabe and M. Kawase, 6-10, PWC publishing (2011)).
20) A. Nonomura, W. Sakai, K. Kinashi, and N. Tsutsumi, "Photorefractive performance of polycarbazoylethylacrylate composite", (Polymer Photonics, and Novel Optical Technologies edited by Y. Kawabe and M. Kawase, 91-95, PWC publishing (2011)).
21) Naoto Tsutsumi, Akihito Dohi, Asato Nonomura, and Wataru Sakai, "Enhanced performance of photorefractive poly(N-vinyl carbazole) composites", *J. Polym. Sci. Part B: Polym. Phys.* **49**, 414-420 (2011).
22) Naoto Tsutsumi, Kazuya Nagata and Wataru Sakai, "Two-photon laser fabrication of three-dimensional silver microstructures with submicron scale linewidth", *Appl. Phys. A* **103**, 421–426 (2011).
23) Naoto Tsutsumi and Hitoshi Nishida, "Tunable Distributed Feedback Lasing with Low Threshold and High Slope Efficiency from Electroluminescent Conjugated Polymer Waveguide", *Optics Commun.* **284**, 3365–3368 (2011).

2012

24) Naoto Tsutsumi and Yuki Nagano, "Off-axis quasi-phase matched second-order optical nonlinearity from $\chi^{(2)}$ gratings induced by holographic all-optical poling", *J. Opt. Soc. Am. B*, **29**(1), 23-28 (2012).

(b) Books

2010

1) W. Sakai and N. Tsutsumi, "Photodegradation and radiation degradation" in "Poly(lactic acid) Synthesis, structures, properties, processing, and applications" edited by R. Auras et al., Chap. 24, 413-422, Wiley (2010).
2) N. Tsutsumi, W. Sakai, "Fundamental Polymer Science (in Japanese)", Saiensu-sha (2010).

2011

1) N. Tsutsumi, "Polymeric Photorefractive Materials (in Japanese)", 【CSJ Current Review 07】in "New Function and Property Based on Polymer-Light Interaction", Part II Chap. 11, 118-123 Kagakudojin (2011).
2) N. Tsutsumi, "Development of Fast Organic Photorefractive Polymers for Advanced Optical Communication Technology (in Japanese)", in "Advanced Photonics Polymer: Materials and Applications", Chap 2, Section 6, 55-60, cmc books (2011).

(c) Reviews and Reports

2007

N. Tsutsumi, “”Fabrication on New Organic Optical Devices with the Structures controlled in the Dimension of Nanometer Scale (in Japanese)”, Function & Materials 27(3), 5-10 (2007).

2008

1) N. Tsutsumi, “Formation of Laser-induced Structure (in Japanese)”, Function & Materials 28(2), 35-42 (2008).
2) N. Tsutsumi, “Organic Laser Devices with Organic Waveguide (in Japanese)”, Expected Materials for the Future 8(8), 48-53 (2008).
3) W. Sakai, “Electron Spin Science & Technology for Polymer Materials - Application of Electron Spin Resonance Measurement - (in Japanese)”, High Polymers, Japan (Kobunshi) 57 (1), 27-30 (2008).

2009

N. Tsutsumi, “Organic Laser Devices (in Japanese)”, Material Stage 9(8), 3-5 (2009).

2012

N. Tsutsumi, “Organic Photorefractive Polymeric Materials (in Japanese)”, Expected Materials for the Future 12(1), 39-44 (2012).

(d) Awards

(e) Invited Lectures

2007

1) N. Tsutsumi, “Hologram Recording and Polymer (in Japanese)”, Kobunshi Doyukai, Society of Polymer Science, Japan, January 22, 2007 (2007).
2) N. Tsutsumi, “Fabrication of Laser Induced Periodic Structures and Geometrical Engineering”, Chemical Society, Japan, March 25, 2008.
3) N. Tsutsumi, W. Sakai, M. Nagta, “Recent Development of Biodegradable Network Polyesters Obtained from Renewable Natural Resources”, The 234th ACS National Meeting, Boston, MA, USA, August, 21, 2007.
4) N. Tsutsumi, “Crystalline Structure, Surface Morphology, and Ferroelectric Response of Ultra-thin Vinylidene Fluoride and Trifluoroethylene Copolymers”, The 2nd International Symposium on Polymer Science, NIST, MD, USA, December 10-12, 2007.
5) N. Tsutsumi, “Fabrication of Laser Induced Periodic Structures and Geometrical Engineering”, 2nd International Symposium on the Manipulation of Advanced Smart Materials (ISMASM2008), Yumebutai, Awaji, May 27-29, 2008.

2010

1) N. Tsutsumi, K. Kinashi, W. Sakai, “Strategy for High Performance Photorefractive Polymer Composites”, 11th Chitose International Forum on Photonics Science & Technology (CIF’11), Chitose, October 14-15, 2010.
2) N. Tsutsumi, K. Kinashi, W. Sakai, “Strategy for High Performance Photorefractive Polymer

Composites and Their Applications to Optical Devices", The 4th International Symposium on Polymer Materials Science, NIST, MD, USA, October 28-29, 2010.

2011

1) N. Tsutsumi, "Photorefractive Polymers - Now and Future -", Polymer Optical Circuit Meetings, Osaka University, March 8, 2011.
2) N. Tsutsumi, "Development of Fast Organic Photorefractive Polymers for Advanced Optical Communication Technology (in Japanese)", Photonics Polymer Meetings, Keio University, June 6, 2011.
3) N. Tsutsumi, K. Kinashi, W. Sakai, "Photorefractive Polymers for Dynamic Holographic Display", 1st Intenational Conference on Advanced Photonic Polymers (ICAPP2011), Yokohama, December 1-2, 2011.

2012

N. Tsutsumi, K. Kinashi, A. Nonomura, W. Sakai, "Quickly Updatable Hologram Images with High Performance Photorefractive Polymer Composites", SPIE Photonics West, San Francisco, CA, USA, January 23-25, 2012.

(f) Patents

2007

1) N. Tsutsumi, M. Urata, K. Iwai, "High molecular weight carbazole contained polymers", Japanese Patent Appl. No. 2007－228568.
2) N. Tsutsumi, Y. Shimizu, "Photorefractive materials and their production methods as well as hologram", Japanese Patent No. 3973964.

2009

N. Tsutsumi, M. Urata, "Photorefractive Composites", Japanese Patent Appl. No. 2009－032004.

2011

N. Tsutsumi, K. Kinashi, Y. Kawabe, J. Nishide, Y. Sasabe, "3 Dimensional holographic displaying system and display devices", Japanese Patent Application No. 2011－259704.

(g) Funds and Financial Supports

2007

N. Tsutsumi, Grant-in-Aid for Scientific Research, Exploratory Research 19655081, "Direct Observation of Temporal Change in Nano-meter Scale Polymer Aggregated Structures Using Two-photon Excited STED Microscopy".

2008

N. Tsutsumi, Grant-in-Aid for Scientific Research, Exploratory Research 19655081, "Direct Observation of Temporal Change in Nano-meter Scale Polymer Aggregated Structures Using Two-photon Excited STED Microscopy".

2009

N. Tsutsumi, N. Moriya, Strategic Promotion of Innovative Research and Development (SPIRE),

200903001, Japan Science and Technology Agency (JST), “Development of Fast Organic Photorefractive Polymers for Advanced Optical Communication Technology”.

2010

N. Tsutsumi, N. Moriya, Strategic Promotion of Innovative Research and Development (SPIRE), 200903001, Japan Science and Technology Agency (JST), “Development of Fast Organic Photorefractive Polymers for Advanced Optical Communication Technology”.

2011

N. Tsutsumi, N. Moriya, Strategic Promotion of Innovative Research and Development (SPIRE), 200903001, Japan Science and Technology Agency (JST), “Development of Fast Organic Photorefractive Polymers for Advanced Optical Communication Technology”.

Polymer Photonics Laboratory

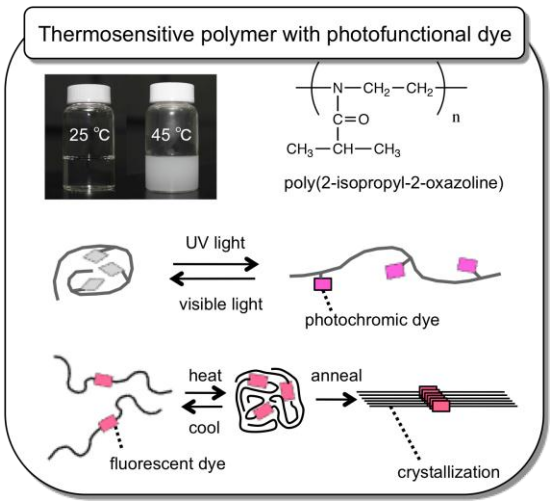
Akira ITAYA, Dr., Prof.

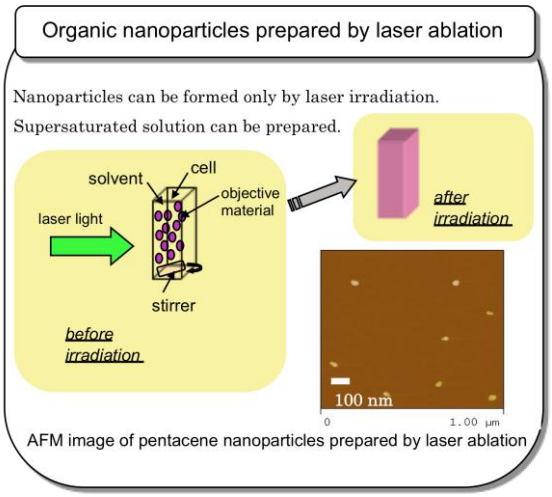
Shinjiro MACHIDA, Dr., Associate Prof.

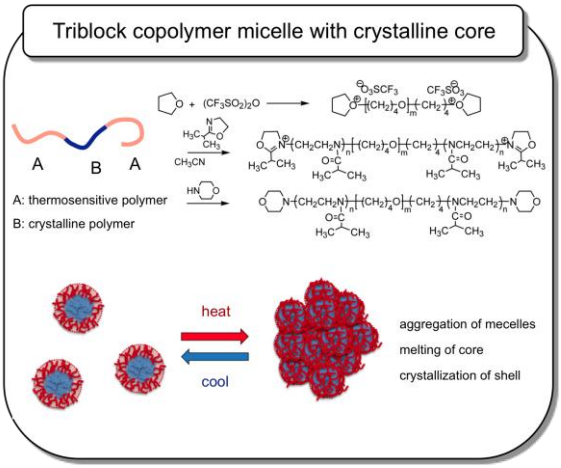
I. Researches

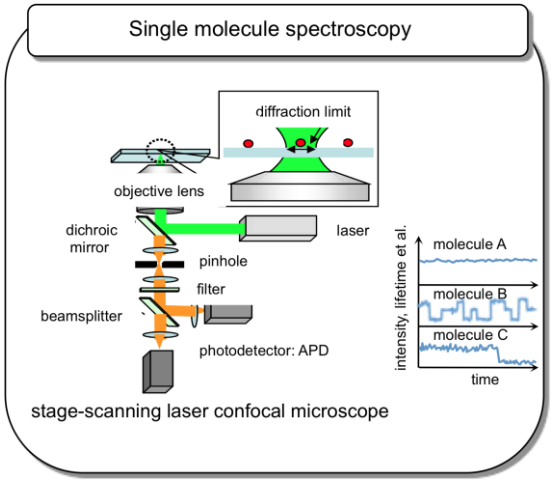
In our laboratory, we are studying photophysical properties of organic materials in nanoscale region and trying to realize novel functional organic or polymer materials by controlling the nanostructure affecting photophysical properties. The key words for our research are "nano" and "photonics". Representative research projects are as follows.

1) Synthesis and characterization of thermosensitive polymers with photofunctional dye
2) Synthesis and micellar characterization of amphiphilic triblock copolymers with crystalline core
3) Transient absorption spectroscopy of organic nanoparticles prepared by laser ablation
4) Nanoscale environments of polymers probed by single molecule spectroscopy
5) Single molecule spectroscopy of charge-transfer (CT) complexes and CT nanocrystals
6) Synthesis and photophysical properties of fluorescent dyes with bulky substituents
7) Transient electric birefringence of polymer solutions and dispersions









II. Publications and Achievements

(a) Original papers

2007

1) S. Machida*, H.Nakata, K. Yamada, and A. Itaya, "Morphological change of a diblock copolymer film induced by selective doping of a photoactive chromophore", *J. Polym. Sci. Part B: Polym. Phys.*, **45**(3), 368-375 (2007).
2) T. Konishi*, K. Kurashiki, A. Itaya, S. Aiba, M. Iwamoto, and Y. Fujii, "Preparation of chitin and chitosan layers by pulsed laser deposition", *Chitin and Chitosan Research*,**13** (1), 1-8 (2007).
3) S. Fukuma, K. Irie, T. Ikegami, S. Masuo, S. Machida, N. Tanaka, and A. Itaya*, "Photophysical and photoconductive properties of a carbazolyl derivative with a mesogen group of alkoxycyanobiphenyl in mesophases", *J. Photochem. Photobiol. A: Chemistry*, **189** (1), 55-64 (2007).
4) S. Masuo*, A. Masuhara, T. Akashi, M. Muranushi, S. Machida, H. Kasai, H. Nakanishi, H. Oikawa, and A. Itaya*, "Photon antibunching in the emission from a single organic dye nanocrystal", *Jpn. J. Appl. Phys.*, **46** (12), L268-L270 (2007).
   Introduced by "RESEACH HIGHLIGHTS" *Nature Photonics*, **1**, 253 (2007).
5) Z. Wang, S. Masuo, S. Machida, and A. Itaya*, "Site-selective doping of dyes into polystyrene-*block*-poly(4-vinylpyridine) diblock copolymer films and selective laser ablation of the dye-doped films" *Jpn. J. Appl. Phys.*, **46** (11), 7569-7576 (2007).

2008

1) S. Machida*, T. Sugihara, S. Masuo, and A. Itaya, "Photoluminescence properties of dye-doped polymer multilayer films with periodic structure", *Thin Solid Films*, **516** (9), 2382-2386 (2008).
2) S. Machida*, T. Wakamatsu, S. Masuo, H. Jinnai, and A. Itaya, "Morphology and photophysical properties of polymer thin films dispersed with dye nanoparticle", *Thin Solid Films*, **516** (9), 2615-2619 (2008).
3) S. Masuo, T. Tanaka, S. Machida, and A. Itaya, "Influence of Molecular Weight and Conformation on Single-Photon Emission from Isolated Conjugated Polymer Chains", *Appl. Phys. Lett.*, **92**(23), 233114 (3 pages) (2008).
4) S. Masuo, T. Endo, Y. Yamane, S. Machida, and A. Itaya*, "Fluorescence Properties of Individual Charge-transfer Complexes in Polymer Films Revealed by Single Molecule Fluorescence Spectroscopy", *Chem. Lett.*, **37**(9), 916-917 (2008).
5) K. Kuwamura, T. Ikegami, S. Masuo, S. Machida, N. Tanaka, and A. Itaya*, "Anomalous excimer formation of a pyrenyl derivative having a mesogen group of alkoxycyanobiphenyl in its smectic mesophase", *J. Photochem. Photobiol. A: Chemistry*, **200**, 232-238 (2008).

2009

1) S. Masuo*, T. Tanaka, T. Murakami, A. Masuhara, S. Machida, H. Kasai, H. Oikawa, and A. Itaya*, "Single-Photon Emission from a Single Nanoparticle Consisting of a Single Conjugated Polymer Chain", *Synthetic Metals*, **159**(9-10), 805-808 (2009).
2) S. Masuo, Y. Yamane, T. Endo, S. Machida, and A. Itaya*, "Fluorescence Dynamics of Individual

Charge-Transfer Complexes in Polymer Films Revealed by Single Molecule Fluorescence Spectroscopy", *J. Phys. Chem. C*, **113**(27), 11590-11596 (2009).

3) S. Masuo, H. Naiki, S. Machida, and A. Itaya, "Photon Statistics in Enhanced Fluorescence from a Single CdSe/ZnS Quantum Dot in the Vicinity of Silver Nanoparticles", *Appl. Phys. Lett.*, **95**(19), 193106 (3 pages) (2009).

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2010

1) A. Itaya*, T. Murakami, N. Yokoi, S. Masuo, and S. Machida, "Laser Ablation of Micro-Sized Organic Dye Particles in Solvents with Limited Solubility for the Dye: Formation of a Supersaturated Solution", *Chem. Lett.*, **39**(3), 215-217 (2010).

2) S. Masuo*, N. Nishi, M. Hosugi, S. Machida, and A. Itaya, "Dependence of Single-photon Emission from Single Conjugated Polymer Chains on Their Spatial Size as Determined by Photon Correlation Measurements in Fluid Solution", *Chem. Lett*., **39**(7), 780-782 (2010).

2011

H. Naiki, S. Masuo*, S. Machida, and A. Itaya*, "Single-Photon Emission Behavior of Isolated CdSe/ZnS Quantum Dots Interacting with the Localized Surface Plasmon Resonance of Silver Nanoparticles", *J. Phys. Chem. C*, **115**(47), 23299-23304 (2011).

2012

S. Masuo, Y. Yamane, S. Machida, and A. Itaya*, "Fluorescence behavior of individual charge-transfer complexes revealed by single-molecule fluorescence spectroscopy: influence of the host polymer matrix", *J. Photochem. Photobiol. A: Chemistry*, **227**, 65-70 (2012).

Online publication complete: 6-DEC-2011, DOI information: 10.1016/j.jphotochem.2011.11.005

(b) Books

1) A. Itaya, S. Machida, and S. Masuo, "Formation of Nanosize Morphology of Dye-Doped Copolymer Films and Evaluation of Organic Dye Nanocrystals Using a Laser", In "Molecular Nano Dynamics" Vol. 1: Spectroscopic Methods and Nanostructures, pp.203-224, (ed. by H. Fukumura, M. Irie, Y. Iwasawa, H. Masuhara, K. Uosaki), Wiley-VCH, Weinheim (2009)

2) S. Masuo, A. Itaya, and S. Machida, "Fabrication of Single-Photon Source using Nano-sizing of Conjugated Polymers (in Japanese)", In "Control of Super-Hierarchical Structures and Innovative Functions of Next-Generation Conjugated Polymers", pp.434-440, (Contributor, K. Akagi), CMC Publisher (2009).

3) S. Machida, "Photo-Hole Burning –Frequency Domain Optical Memory (in Japanese)", In "Subject-Book of Photochemistry" (ed. by S. Ito, M. Sisido, K. Horie, T. Majima), Asakura Shoten (in press).

4) A. Itaya, "Excimer and Exciplex (in Japanese)", In "Subject-Book of Photochemistry" (ed. by S. Ito, M. Sisido, K. Horie, T. Majima), Asakura Shoten (in press).

(c) Reviews and Reports

2008

S. Masuo and A. Itaya, "Antibunching Emission from a Single Organic Dye Nanocrystal (in Japanese)", Optics, **37**, 472-474 (2008).

2011

S. Masuo, H. Naiki, T. Tanaka, S. Machida, and A. Itaya, "Photon Antibunching Behavior of a System Consisting of Nano-sized Fluorophore and Metal Nanostructure (in Japanese)", Molecular Electronics and Bioelectronics, **22**, 127-132 (2011).

(d) Awards

(e) Invited Lectures

(f) Patents

(g) Funds and Financial Supports

2007-2008

S. Masuo, A. Itaya, and S. Machida, Grant-in-Aid for Scientific Research on Priority Areas, #446, "Fabrication of Single-Photon Source using Nano-sizing of Conjugated Polymers"

2007-2010

A. Itaya, Joint Research with Nissan Chemical Industries Limited, "Studies on Photo- and Electronic-Functional Polymeric and Organic Materials"

2009-2011

A. Itaya and S. Masuo, Grant-in-Aid for Scientific Research, Scientific Research (C) 21550012, "Studies on Isolated Charge-Transfer Complexes and Charge-Transfer Complexes Nanocrystals using Single Molecule Fluorescence Spectroscopy"

Polymer Physics Laboratory
Shu HOTTA, Dr., Prof.
Takeshi YAMAO, Dr., Associate Prof.

I. Researches

We are currently developing a novel series of organic semiconductors. We term these semiconductors "**thiophene/phenylene co-oligomers (TPCOs)**." The TPCOs comprise thiophenes and phenylenes (benzenes) that are widely used as raw materials of dyes and pharmaceutical agents. These TPCOs exhibit a number of unique and interesting optoelectronic and semiconducting characteristics. We mention them as below.

(i) Various molecular backbones bent, zigzag, pseudo-straight, a bird's wing, etc. can readily be shaped. These variations result from appropriately arranging the *pentagonal* thiophenes and *hexagonal* phenylenes in the molecule (see Fig. 1). Non-straight molecules produce a peculiar crystallographic structure where the molecular long axes stand nearly upright against the bottom crystal plane. This crystal structure is responsible for high-performance electronic and photonic characteristics of the TPCOs. Examples include high carrier mobility (~1 cm^2/Vs) and spectrally-narrowed emissions (SNEs), e.g. amplified spontaneous emission (ASE), laser oscillation, stimulated resonant Raman scattering, etc.

(ii) Regarding the industrial applications, it will be highly advantageous that the emission colors can subtly be tuned. This can readily be achieved by changing the total ring number of thiophenes and phenylenes and their arrangement in a molecule. These compounds are accessible via organosynthetic routes such as Suzuki coupling

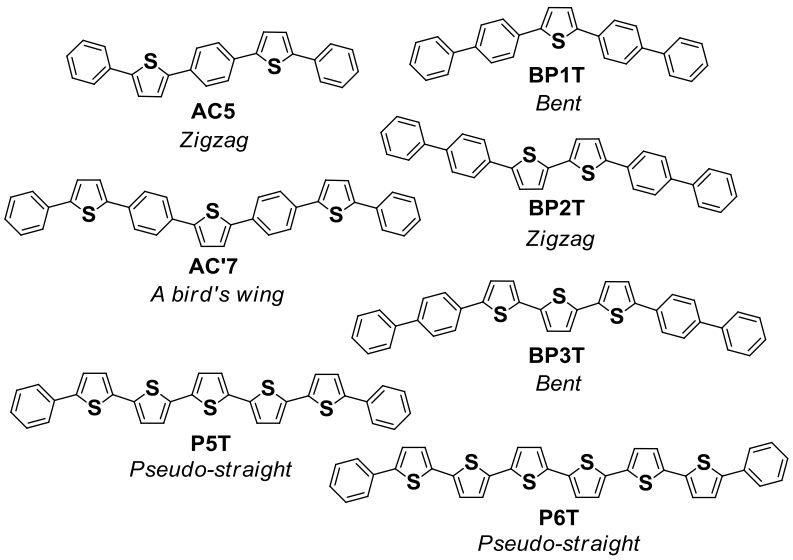

Fig. 1. Various thiophene/phenylene co-oligomers (TPCOs) and their molecular shapes (bent, zigzag, pseudo-straight, a bird's wing, etc.).

and Grignard coupling. Thus the TPCOs are attractive and promising in both the basic research and technological aspects.

(iii) Another advantage lies in that the TPCO molecules can be chemically-modified at either molecular terminal. This is particularly useful in controlling polarity of the semiconductor (i.e. either the p-type or the n-type). To this end we use e.g. alkyl and methoxy groups for the p-type materials and fluorine, trifluoromethyl groups, cyano groups, etc. for the n-type. Both types of materials are indispensable constituents of the semiconductor devices.

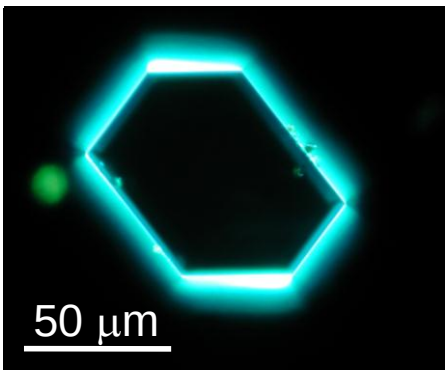

Fig. 2. Fluorescence micrograph of a BP1T crystal grown in a liquid phase.

We also developed growth methods of thin single crystals of TPCOs and other organic semiconductors. As an example Fig. 2 shows a micrograph of a hexagon single crystal of BP1T. The contrast between glaring edge emissions and complete darkness inside the crystal reflects the exceedingly effective optical confinement in the crystal. Superior ability of this optical confinement is one of attractive characteristics of the TPCOs and makes their crystals an excellent candidate for a material of organic light-emitting devices and laser media.

II. Publications and Achievements

(a) Original papers

2007

1) S. Hotta, M. Goto, and R. Azumi, "Peculiar Crystal Structure of a Thiophene/Phenylene Co-Oligomer of 2,5-Bis(4'-methoxybiphenyl-4-yl)thiophene," *Chem. Lett*. **36**, 270–271 (2007).
2) K. Yamane, H. Yanagi, A. Sawamoto, and S. Hotta, "Ambipolar Organic Light Emitting Field Effect Transistors with Modified Asymmetric Electrodes," *Appl. Phys. Lett*. **90**, 162108/3 pages (2007).
3) T. Yamao, T. Ohira, S. Ota, and S. Hotta, "Polarized Measurements of Spectrally Narrowed Emissions from a Single Crystal of a Thiophene/Phenylene Co-Oligomer," *J. Appl. Phys*. **101**, 083517/5 pages (2007).
4) T. Katagiri, S. Ota, T. Ohira, T. Yamao, and S. Hotta, "Synthesis of Thiophene/Phenylene Co-Oligomers. V. Functionalization at Molecular Terminals toward Optoelectronic Device Applications," *J. Heterocyclic Chem*. **44**, 853–862 (2007).
5) S. Fujiwara, K. Bando, Y. Masumoto, F. Sasaki, S. Kobayashi, S. Haraichi, and S. Hotta, "Laser Oscillations of Whispering Gallery Modes in Thiophene/Phenylene Co-Oligomer Microrings," *Appl. Phys. Lett*. **91**, 021104/3 pages (2007).
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9) T. Yamao, K. Yamamoto, Y. Taniguchi, and S. Hotta, "Spectrally Narrowed Emissions Occurring near an Interface between a Single Crystal Thiophene/Phenylene Co-Oligomer and a Glass Substrate," *Appl. Phys. Lett.* **91**, 201117/3 pages (2007).

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1) K. Bando, T. Nakamura, S. Fujiwara, Y. Masumoto, F. Sasaki, S. Kobayashi, Y. Shimoi, and S. Hotta, "Optical Selection Rule for the Lower Davydov Excitons in Co-Oligomer Single Crystals," *Phys. Rev. B* **77**, 045205/6 pages (2008).
2) T. Shimada, S. Hotta, and H. Yanagi, "Energy-Transferred Photoluminescence from Thiophene/Phenylene Oligomer Thin Films," *J. Lumin*. **128**, 457–461 (2008).
3) T. Yamao, S. Ota, T. Miki, S. Hotta, and R. Azumi, "Improved Sublimation Growth of Single Crystals of Thiophene/Phenylene Co-Oligomers," *Thin Solid Films* **516**, 2527–2531 (2008).
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5) K. Yamane, A. Sawamoto, S. Hotta, and H. Yanagi, "Organic Heterojunction Ambipolar Field Effect Transistors with Asymmetric Source and Drain Electrodes," *Thin Solid Films* **516**, 2758–2761 (2008).
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7) T. Yamao, T. Inoue, Y. Okuda, T. Ishibashi, S. Hotta, and N. Tsutsumi, "Gain-Narrowed Emissions from Oligomer Crystals Assisted by Interference Exposure," *Synth. Met*. **159**, 889–892 (2009).
8) S. Z. Bisri, T. Takenobu, Y. Yomogida, H. Shimotani, T. Yamao, S. Hotta and Y. Iwasa, "High Mobility and Luminescent Efficiency in Organic Single-Crystal Light-Emitting Transistors," *Adv. Funct. Mater*. **19**, 1728–1735 (2009).
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3) T. Yamao, Y. Shimizu, H. Kuriki, T. Katagiri, and S. Hotta, "Improved Field-Effect Transistor Characteristics of an n-Type Semiconducting Thiophene/Phenylene Co-Oligomer," *Jpn. J. Appl. Phys.* **49**, 01AB01/4 pages (2010).
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10) F. Sasaki, M. Mori, S. Haraichi, Y. Ido, Y. Masumoto, and S. Hotta, "Microdisk Lasers and Field Effect Transistors of Thiophene/Phenylene Co-Oligomers by Using High Temperature Deposition Method," *Org*. *Electron*. **11**, 1192–1198 (2010).
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15) K. H. K. Chan, T. Yamao, M. Kotaki, and S. Hotta, "Unique Structural Features and Electrical Properties of Electrospun Conjugated Polymer Poly(3-hexylthiophene) (P3HT) Fibers," *Synth. Met*. **160**, 2587–2595 (2010).

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2) H. Yanagi, Y. Marutani, F. Sasaki, Y. Makino, T. Yamao, and S. Hotta, "Prethreshold Lasing with Time-Delayed Pulse Emission from a Single Crystal of Thiophene/Phenylene Co-Oligomer," *Appl. Phys. Express* **4**, 062601/3 pages (2011).
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(b) Books

2007

S. Hotta, "Organic Transistors (in Japanese)," 46 pages, ED Research (2007).

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2010

1) S. Hotta, in "Organic Semiconductor Device – From Fundamentals to the Latest Materials and Devices (in Japanese)," pp. 171–175, pp. 299–300, (ed. by 142 Committee of Japan Society for the Promotion of Science), Ohmsha (2010).
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T. Yamao and T. Horiguchi, in "Development of Highly Efficient Two-Photon Absorption Materials and their Applications (in Japanese)," pp. 85–89, (ed. by T. Watanabe), CMC Publishing (2011).

(c) Reviews and Reports

2008

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2011

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(d) Awards

(e) Invited Lectures

2009

1) T. Yamao, K. Terasaki, Y. Shimizu, and S. Hotta, "Light Emission from Organic Field-Effect Transistors Enhanced by Alternating-Current Gate Voltages," IMR Workshop on Organic Light Emitting Devices, Japan (2009).
2) H. Yanagi, F. Sasaki, and S. Hotta, "Light Amplification by Stimulated Resonant Raman Scattering in Organic Solids," IMR Workshop on Organic Light Emitting Devices, Japan (2009).
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2010

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2) S. Hotta, "The Thiophene/Phenylene Co-Oligomers: High-Performance Molecular Semiconductors Integrating Electronic and Optical Functionalities," 2010 International Chemical Congress of Pacific Basin Societies (PACIFICHEM 2010), U. S. A. (2010).

(f) Patents

2007

S. Bando, T. Katagiri, M. Miyata, M. Suzuki, H. Kitayama, S. Hotta, and T. Yamao, "(Thiopene/Phenylene) Co-Oligomer," Japanese Patent Appl. No. 2007-285196, Publication No. JP,2009-114074,A.

2008

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2009

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2010

1) H. Kanbara, N. Koshobu, J. Kobayashi, T. Yamao, and S. Hotta, "Electrooptic Waveguide and Electrooptic Element Using the Same," Japanese Patent Appl. No. 2010-186649.
2) S. Hotta, T. Yamao, K. Terasaki, A. Okada, and K. Kajiwara, "Light-Emitting Transistor Including Organic Laminate," Japanese Patent Appl. No. 2010-248628, Publication No. JP,2011-187924,A.

2011

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(g) Funds and Financial Supports

2007

S. Hotta, Grant-in-Aid for Scientific Research on Priority Areas "Super-Hierarchical Structures," No. 17067009, "Ultimate Performance of Hybridized Conjugated Polymers with Super-Controlled Sizes and Molecular Shapes," The Ministry of Education, Culture, Sports, Science and Technology.

2008

1) S. Hotta, Grant-in-Aid for Scientific Research on Priority Areas "Super-Hierarchical Structures," No. 17067009, "Ultimate Performance of Hybridized Conjugated Polymers with Super-Controlled Sizes and Molecular Shapes," The Ministry of Education, Culture, Sports, Science and Technology.
2) T. Yamao, Grant-in-Aid for Exploratory Research, No. 20655041, "Linearly Polarized and Single Mode Laser Oscillations from Hexagonal Organic Single Crystals," The Ministry of Education, Culture, Sports, Science and Technology.

2009

1) T. Yamao, Grant-in-Aid for Challenging Exploratory Research, No. 20655041, "Linearly Polarized and Single Mode Laser Oscillations from Hexagonal Organic Single Crystals," The Ministry of Education, Culture, Sports, Science and Technology.
2) T. Yamao Grant for Basic Science Research Projects, "Current-Excited Laser Oscillations from

Organic Crystal Devices," The Sumitomo Foundation.

2010

1) S. Hotta, Grant-in-Aid for Scientific Research (B), No. 22350082, "Development of Oligomer Semiconductor Laser Devices Based on Crystal Engineering," The Ministry of Education, Culture, Sports, Science and Technology.
2) T. Yamao, Grant for Basic Science Research Projects, "Current-Excited Laser Oscillations from Organic Crystal Devices," The Sumitomo Foundation.
3) T. Yamao, Research Grant, "Understanding of Current-Induced Light-Emissions by Alternating-Current Voltage Application to Gate Electrodes of Organic Field-Effect Transistors," The Mazda Foundation.

2011

1) S. Hotta, Grant-in-Aid for Scientific Research (B), No. 22350082, "Development of Oligomer Semiconductor Laser Devices Based on Crystal Engineering," The Ministry of Education, Culture, Sports, Science and Technology.
2) T. Yamao, Grant-in-Aid for Scientific Research (C), No. 23550208, "Fabrication and Understanding of Solid State Lasers Based on Layered Organic Crystals with a p-n Junction," The Ministry of Education, Culture, Sports, Science and Technology.
3) T. Yamao, Research Grant, "Understanding of Current-Induced Light-Emissions by Alternating-Current Voltage Application to Gate Electrodes of Organic Field-Effect Transistors," The Mazda Foundation.
4) T. Yamao, Research Grant, "Development of a Phase-Resolved Measurement System for Current and Emission of Organic Light-Emitting Transistors Operated by Alternating-Current Gate Voltages," The Murata Science Foundation.

2012

1) T. Yamao, Grant-in-Aid for Scientific Research (C), No. 23550208, "Fabrication and Understanding of Solid State Lasers Based on Layered Organic Crystals with a p-n Junction," The Ministry of Education, Culture, Sports, Science and Technology.
2) T. Yamao, Research Grant, "Development of a Phase-Resolved Measurement System for Current and Emission of Organic Light-Emitting Transistors Operated by Alternating-Current Gate Voltages," The Murata Science Foundation.

Polymer Molecular Engineering Laboratory
Qui. TRAN-CONG-MIYATA, Dr., Prof.
Tomohisa NORISUYE, Dr., Associate Prof.

I. Researches

The main aim of researches in our Polymer Molecular Engineering (PME) Lab is designing polymer materials with novel physical properties using chemical reactions and is also developing novel characterization methods for polymers engineering and science. The final goal is constructing polymers with novel properties which have ever been challenged and achieved before. Designing polymers are mainly based on conventional methods such as sol-gel techniques and photo-polymerization. The characterization methods cover the broad range of structure analysis for polymers ranging from transparent to visible light to translucent and completely turbid. As the main part of materials characterization, structure analysis are studied using both real space experimental techniques such as microscopy (phase-contrast, interference, reflection, fluorescence, laser-scanning confocal microscopy) and measurements using reciprocal space (light scattering, ultrasonics scattering and interferometry). The most recent achievements of our group are summarized as follows:

1. Controlling Morphologies of Polymer Mixtures by Photochemical Reactions

Ordered structures in Nature are naturally created by the spontaneous competition processes among many antagonistic driving forces over a very long period of time. These competition processes occur at various length scales ranging from a few millimeters to few hundred thousand kilometers over a large range of time scales, leading to a wide variety of hierarchical structures. In the laboratory scales, in order to generate and control morphology of polymeric materials, we have coupled various photochemical reactions to the phase separation process of polymer mixtures. Reactions performed in these experiments are either photo-cross-link using photodimerization of anthracene derivatives or photoisomerization of stilbene and azobenzene. By taking advantages of these competing interactions during phase separation, intermediate periodic morphologies can be generated and stabilized by irradiation with UV light. So far, as illustrated in Fig. 1, the following morphologies were generated with this *"competing interactions strategy"*: *bi-continuous* morphologies, *tri-continuous* morphologies, *spatially graded continuous* morphologies, *hexagonal phases*, *hierarchical* morphologies, *three-dimensional (3D) salami* structures etc.

As for practical application, we were successful in selectively dispersing nanofillers such as multi-walled carbon nanotubes (MWCNTs) in a minor component of a polymer blend with continuous morphology by reaction-induced phase separation. These experimental results clearly reveal the *insulating-conducting transition* phenomena in synthetic polymers drivable by phase separation and also open a new route to design and produce conducting materials using the composites of synthetic polymers and nanofillers such as carbon nanotubes. An example for a 3D networks of CTNs in polymers is illustrated in Figure 2.

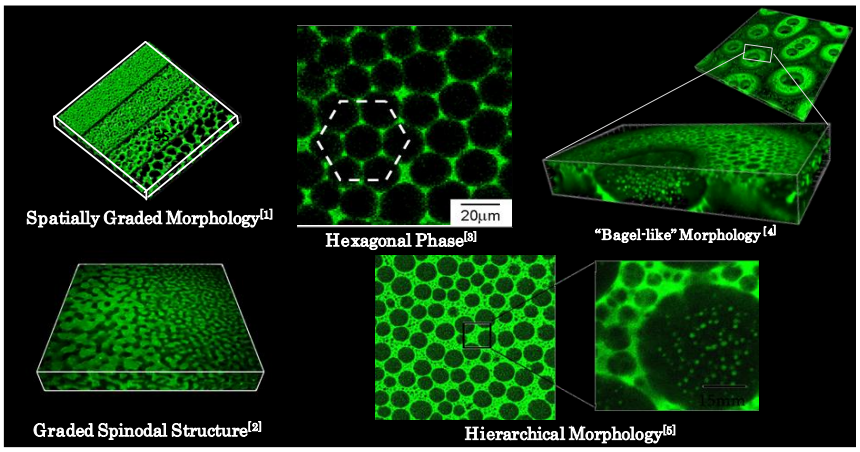

Fig.1. *Various hierarchical and co-continuous morphologies resulting from the competitions between photochemical reactions and phase separation.*

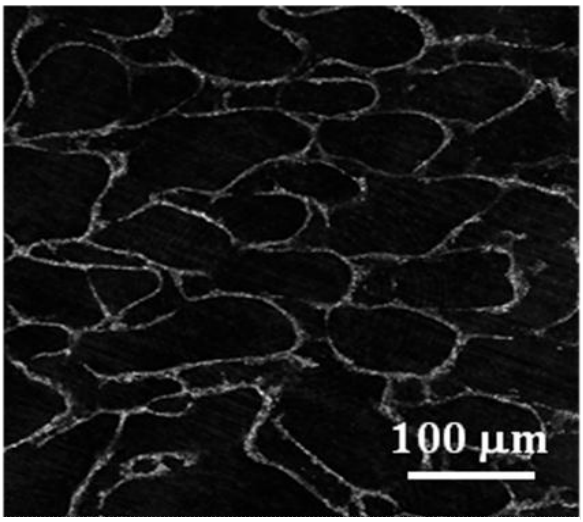

Fig. 2. MWCNTs networks in a polymer composite imaged by reflection mode of laser-scanning confocal microscopy.

2. Newer Characterization Methods for Polymer Materials

a) *in situ* Monitoring the Local Deformation of Polymer Films in the Nanometer Scales

For most polymeric systems, inducing a chemical reaction between polymer chains in the bulk state often generates a local strain field, leading to a local deformation. This local strain field could critically affect the physical properties of the reacting polymer materials. Depending upon the distance from the glass transition temperature, this local (microscopic) strain field would relax instantaneously or persist over a long period of time. We have developed a Mach-Zehnder interferometric (MZI) system shown in Fig. 3 to *in situ* monitor this reaction-induced elastic strain and its relaxation process in a photo-reactive polymers. The 2D (planar) deformation in the nanometer scales observed for a photocured polymer is illustrated in Fig. 3 during the course of irradiation.

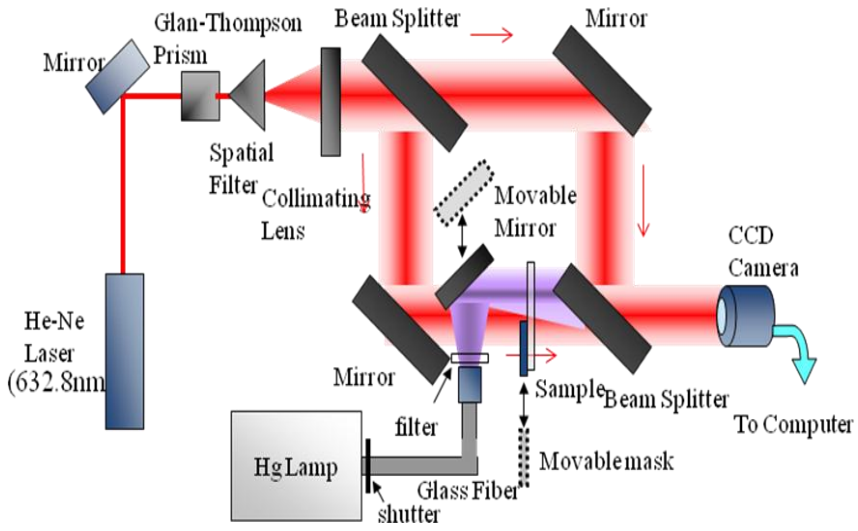

Fig. 2. *Block diagram of the Mach-Zehnder interferometer.*

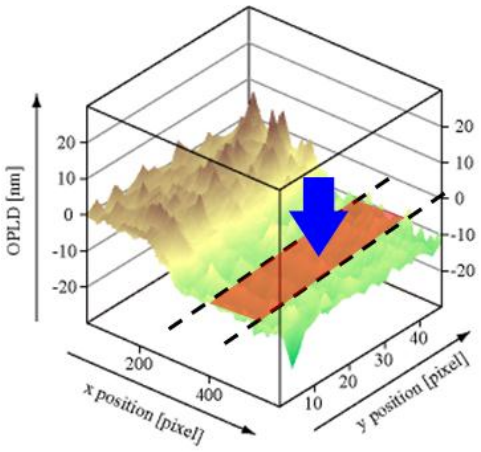

Fig. 3. *Imaging the 2D deformation obtained from the Mach-Zehnder interferometric data.*

b) Dynamic Ultrasound Scattering (DSS) Method

Since characterization method using light would be unavailable for turbid samples, particularly for multi-phase polymer materials, ultrasound becomes an indispensible tool to characterize these phase-separated samples. The concept and the apparatus of the DSS method are illustrated in Fig. 4.

Unlike light scattering, it is able to obtain, besides the scattering intensity, the phase information with this DSS scattering techniques. This important information enables us to additionally obtain the dynamics of the system as a function of position in the sample. As an example, by the DSS techniques, the cooperative motions of micron-sized particles in the presence of long-ranged hydrodynamic interactions in aqueous suspensions can be evaluated to elucidate not only the particle size but also their distribution using the data of velocity field. As shown in Fig. 5, we have demonstrated that the complicated dynamics of particles spontaneously undergoing sedimentation and floating can be successfully distinguished and visualized by using the *phase-mode* dynamic ultrasound techniques .

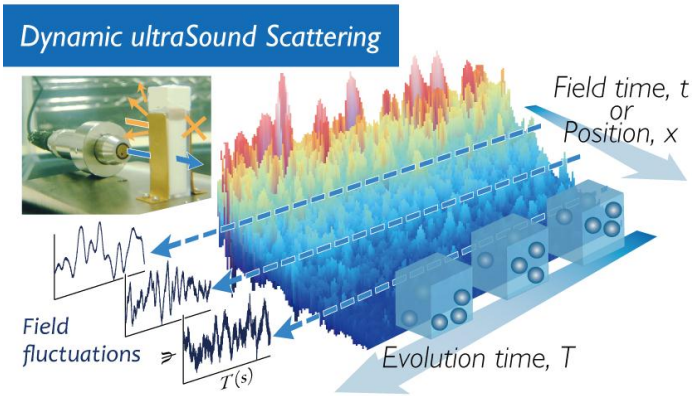

Fig. 4. *Instrumentation and the concept of observing fluctuations by dynamic ultrasound scattering (DSS).*

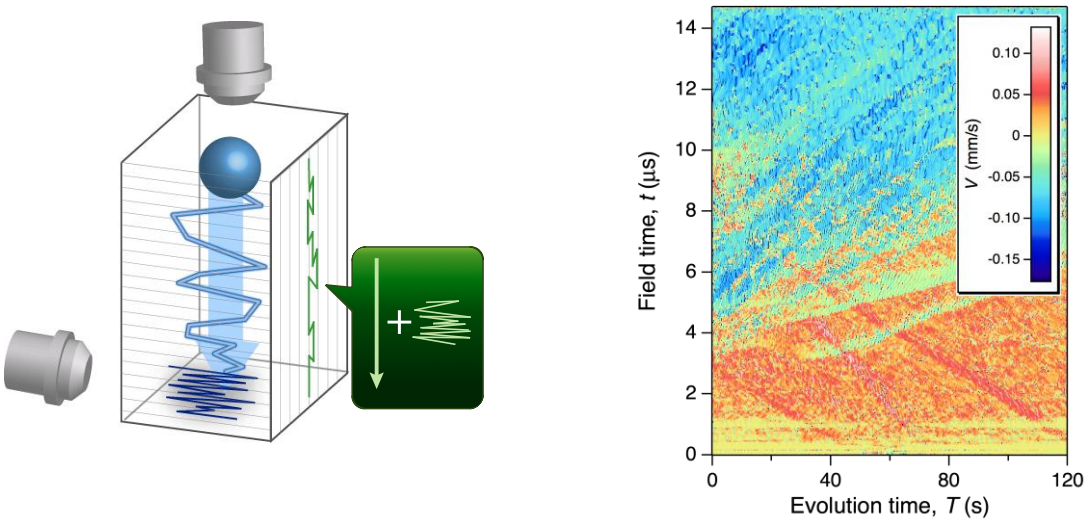

Fig. 5. *Multi-directional monitoring (left) and imaging (right) of particles spontaneously undergoing floating and sedimentation in a suspension liquid using the phase-mode dynamic ultrasound scattering (DSS).*

II. Publications and Achievements

(a) Original papers

2007

1) Hironobu Hori, Osamu Urakawa, Okimichi Yano, Qui Tran-Cong-Miyata, *"*Phase Separation of Binary Polymer Mixtures Under an Electric Field*"*, *Macromolecules*, **40**, 389 – 394 (2007).
2) X.-A. Trinh, J. Fukuda, Y. Adachi, H. Nakanishi, T. Norisuye and Q. Tran-Cong-Miyata, "Effects of Elastic Deformation on Phase Separation of a Polymer Blend Driven by a Reversible Photo-Cross-Linking Reaction", *Macromolecules*, **40**, 5566-5574 (2007).
3) Y. Takata, T. Norisuye, S. Hirayama, T. Takemori, Q. Tran-Cong-Miyata and S. Nomura, "DLS and AFM Studies on the Cluster Evolution of Organically Modified Silica Gels Catalyzed by a Super Strong Acid", *Macromolecules*, **40**, 3773-3778 (2007).
4) T. Nakanishi, T. Norisuye, H. Sato, Q. Tran-Cong-Miyata, S. Nomura and T. Sugimoto, *"*Studies on Microscopic Structure of Sol-Gel Derived Nanohybrids Containing Heteropolyacid", *Macromolecules*, **40**, 4165-4172 (2007).
5) H. Sato, T. Norisuye, T. Takemori, Q. Tran-Cong-Miyata and S. Nomura, *"*Effects of Solvent on Microstructure and Proton Conductivity of Organic-Inorganic Hybrid Membranes*"*, *Polymer*, **48**, 5681-5687 (2007)
6) A. Masunaga, Soh Ishino, H. Nakanishi, Q. Tran-Cong-Miyata, *"*Phase Separation Kinetics and Morphology of Light-Induced Interpenatrating Polymer Networks (IPNs) Confined in the Micrometer Scales (in Japanese)*"*, *Japanese J. Polym. Sci. Tech.* (*Kobunshi Ronbunshu*), **64**, 294 - 300 (2007).

2008

1) H. Nakanishi, M. Satoh, Q. Tran-Cong-Miyata, "Hexagonal Phase Induced by a Reversible Photo-cross-link Reaction in a Polymer Mixture", *Phys. Rev. E Rapid Commun.*, **77**, 020801(R) (2008).
2) T. Norisuye, Y. Ikezawa, T. Takemori, Q. Tran-Cong-Miyata and S. Nomura, "Studies on Structural Characterization of Organic-Inorganic Proton Conductive Membranes (in Japanese)", *Japanese J. Polym. Sci. Tech.* (*Kobunshi Ronbunshu*), **65**, 716 - 729 (2008).
3) M. Kohyama, T. Norisuye, Q. Tran-Cong-Miyata, "High Frequency Dynamic Ultrasound Scattering from Microsphere Suspensions", *Polymer J.*, **40**, 398-399 (2008).

2009

1) Q. Tran-Cong-Miyata, D.-T. Van-Pham, K. Noma, T. Norisuye , H. Nakanishi, "The roles of Reaction Inhomogeneity in Phase Separation Kinetics and Morphology of Reacting Polymer Blends", *Chinese J. Polym. Sci.*, **26**, 23-36 (2009).
2) D.-T. Van-Pham, K. Sorioka, T. Norisuye, Q. Tran-Cong-Miyata, "Physical Aging of Photo-Crosslinked Poly(ethyl acrylate) Observed in the Nanometer Scales by Mach-Zehnder Interferometry", *Polymer J.*, **41**, 260-265 (2009)
3) Mariko Kohyama, Tomohisa. Norisuye, Qui Tran-Cong-Miyata, "Dynamics of Microsphere Suspensions Probed by High Frequency Dynamic Ultrasound Scattering", *Macromolecules*, **42**,

752-759 (2009)

4) Kosuke Murata, Tasuku Murata, Hideyuki Nakanishi, Tomohisa Norisuye and Qui Tran-Cong-Miyata* "Effects of Light-Driven Regularity on the Physical Properties of Multiphase Polymers", *Macromol. Mater. Eng.*, **294**, 163-168 (2009).
5) A. Nagao, M. Kohyama, T. Norisuye, Q. Tran-Cong-Miyata, "Simultaneous Observation and Analysis of Sedimentation and Floating Motions of Microspheres Investigated by Phase Mode-Dynamic Ultrasound Scattering*", J. Appl. Phys.*, **105**, 023526 (2009).
6) M. Fukuoka, H. Nakanishi, T. Norisuye, Q. Tran-Cong-Miyata, "Light Scattering Study on the Mode-Selection Process in Reversible Phase Separation of a Photoreactive Polymer Mixture*",* *J. Phys. Chem. B,* **113**, 14950-14956 (2009)

2010

1) R.R. Nigmatullin, K. Fukao, H. Nakanishi, Q. Tran-Cong-Miyata, D. Tahara and K. Fukao, "Application of New Treatment Methods for Reading of Random Sequences: a Quantitative Description of Aging Phenomena in Polymer Glasses", *Commun. Nonlinear Sci. Numer. Simul.*, **15**, 1286-1307 (2010)
2) D.T. Van-Pham, X.-A. Trinh, H. Nakanishi, Q. Tran-Cong-Miyata, "Design and Morphology Control of Polymer Nanocomposites Using Light-Driven Phase Separation Phenomena", *Adv. Nat. Sci. Nanosci. Nanotech.*, **1**, 013002 (2010).
3) Daisuke Fujiki, Chuanming Jing, Dan-Thuy Van-Pham, Hideyuki Nakanishi, Tomohisa Norisuye and Qui Tran-Cong-Miyata, "Polymer Materials with Spatially Graded Morphologies: Preparation, Characterization and Utilization", *Adv. Nat. Sci*., **1**, 043003 (2010).

2011

1) T. Norisuye, S. Sasa, K. Takeda, M. Kohyama, Q. Tran-Cong-Miyata, "Simultaneous Evaluation of Ultrasound Velocity, Attenuation and Density Polymer Solutions Observed by Multi-echo Ultrasound by Multi-echo Ultrasound Spectroscopy", *Ultrasonics*, **51**, 215-222 (2011).
2) D.-T. Van-Pham, K. Sorioka, T. Norisuye and Q. Tran-Cong-Miyata, "Formation and Relaxation of the Elastic Strain Generated by Photocuring in Polymer Blends Monitored by Mach-Zehnder Interferometry", *Polymer*, **52**, 739-745 (2011)
3) K. Kinohira, D.-T. Van-Pham, A. Hirose, T. Norisuye, Q. Tran-Cong-Miyata, " Phase Separation of Polymer Mixtures Driven by Photochemical Reactions: Complexity and Fascination", *Current Opinion in Solid State and Materials Science*, **15**, 254-261 (2011)
4) K.-M. Nie, C.-M. Jing, H. Nakanishi, T. Norisuye, Q. Tran-Cong-Miyata, "Photoreaction-induced Phase Separation and Morphology Control in Ternary IPNs Blends Involving 3D Spherical Dendrimer", *Soft Matter*, **7**, 10556-10560 (2011)

(b) Books

2009

1) Q. Tran-Cong-Miyata and H. Nakanishi, "Pattern Formation Induced by Chemical Reactions in Polymeric Systems (in Japanese)" in "Handbook of Self-Organization", T. Kunitake, M.

Shimomura, T. Yamaguchi Eds., NTS Publishing Company, Tokyo, pp. 249-252 (2009).

2) H. Nakanishi, T. Norisuye and Q. Tran-Cong-Miyata,"Morphosynthesis in Polymeric Systems Using Photochemical Reactions" in "Molecular Nano Dynamics" Vol. I, H. Fukumura et al. Eds., Chapter 10, Wiley-VCH, Weinheim, pp. 173-186 (2009).

3) Q. Tran-Cong-Miyata and H. Nakanishi, "Phase Separation and Morphology of Polymer Mixtures Driven by Light" in "Polymers, Liquids and Colloids in Electric Fields", Y. Tsori and U. Steiner Eds., Chapter 6, World Scientific, London, pp. 171 – 195 (2009).

2010

1) I. R. Epstein, John A. Pojman and Q. Tran-Cong-Miyata, "What is Nonlinear Dynamics and How Does it Relate to Polymers?", in "Nonlinear Dynamics with Polymers: Fundamentals, Methods and Applications", J.A. Pojman and Q. Tran-Cong-Miyata Eds., Chapter 2, Wiley-VCH, Weinheim, pp. 5- 19 (2010).

2) H. Nakanishi, D. Fujiki, D.-T. Van-Pham and Q. Tran-Cong-Miyata, "Reaction-Induced Phase Separation of Polymeric Systems under Stationary Nonequilibrium Conditions" in "Nonlinear Dynamics with Polymers: Fundamentals, Methods and Applications", J.A. Pojman and Q. Tran-Cong-Miyata Eds., Chapter 6, Wiley-VCH, Weinheim, pp. 276-290 (2010).

(c) Reviews and Reports

2009

H. Nakanishi and Q. Tran-Cong-Miyata, "Light-Induced Self-Ordering Phenomena in Polymer Mixtures (in Japanese)", Kobunshi High Polymers, Japan (published by the Society of Polymer Science, Japan), Vol. **58** (No.7), 465-468 (2009).

(d) Awards

2010

D.-T. Van-Pham, T. Kinohira, Y. Arao, T. Norisuye and Q. Tran-Cong-Miyata, "Studies on Elastic Strain and Its Relaxation Behavior in Photo-Cross-Linked Polymeric Systems Observed by Mach-Zehnder Interferometry", Students Poster Awards, International Symposium on Polymer Physics, Ji-Nan, Shangdong, China**,** June 6-10 (2010).

(e) Invited Lectures

2007

1) Q. Tran-Cong-Miyata,"Reaction-Induced Elastic Deformation and Its Influence on Thermodynamic Instabilities of Polymer Networks", Lecture at the Cargèse Summer School on "Morphogenesis through the Interplay of Nonlinear Chemical Instabilities and Elastic Active Media", Institut d'Études Scientifiques de Cargèse, Corsica, France, July 2-14, 2007.

2) Q. Tran-Cong-Miyata, "How far Can We Control Morphology of Polymer Blends by Using Chemical Reactions ?", Invited talk at "The Second International Symposium on Polymer Materials Science", National Institute of Standards and Technology, Gaithersburg, Maryland,

U.S.A., December 10-11, 2007.

2008

1) Q. Tran-Cong-Miyata, “Co-continuous Morphology Resulting from Competing Interactions in Reacting Polymer Blends and Its Practical Implication”, Invited Talk at the Materials Research Science and Engineering Center (MRSEC), Northwestern University, April 4 (2008), Illinois, USA.
2) Q. Tran-Cong-Miyata, “Competing Interactions and Pattern Selection Driven by Chemical Reactions in Polymer Mixtures”, Invited Talk at The 235th American Chemical Society, Division of Polymer Materials Science (PMSE), April 6-10 (2008), New Orleans, U.S.A.

2009

Q. Tran-Cong-Miyata, “Co-continuous Morphologies of Polymer Blends: Generation, Design and Application”, Invited Talk at The 5th JSPS Seminar on Asia-Africa Science Platform Program on Neo-Fiber Technology, July 20-23 (2009), Ha-Noi University of Technology, Ha-Noi, Viet-Nam.

2010

1) Q. Tran-Cong-Miyata, “Polymers with Spatially Graded Continuous Morphology Generated by Phase Separation under Spatially Non-uniform Conditions”, Invited Talk at the International Symposium on Polymer Physics (PP-2010), June 6-10, 2010 Ji’nan, China.
2) Q. Tran-Cong-Miyata, "Light-Induced Phase Separation in Polymer Mixtures as a Pattern-Formation Process: Complexity and Fascination", Invited Talk at the “Non-linear Dynamics and Self-Organization in Chemical Systems”, 18 – 20, October (2010) – Centre de Recherche Paul Pascal, Bordeaux, France.
3) Q. Tran-Cong-Miyata, “Some Recent Findings in Phase Separation of Reacting Polymer Mixtures”, Invited Talk at The 4th International Symposium on Polymer Materials Science, National Institute of Technology (NIST), Gaithersburg, Maryland, USA, October 28-29 (2010).

2011

1) Q. Tran-Cong-Miyata, “Phase Separation of Photo-reactive Polymer Mixtures:Complexity and Fascination”, High Polymer Research Group Conference “Stimuli Responsive and Reactive Polymer Systems”, Pott Shrigley, United Kingdom, April 17-21 (2011).
2) T. Norisuye, "Dynamics of microsphere suspensions observed by ultrasound technique", Tokai Polymer Student Forum, sponsored by The Society of Polymer Science, Tokai Branch, Japan, Nagoya, March 5th (2011).
3) T. Norisuye, "Dynamics of Microspheres Suspension Observed by Dynamic Ultrasound Scattering", 56th Symposium on Acoustics and Physics, Kyoto, July 28 (2011)
4) T. Norisuye, "Dynamics of microsphere suspensions by dynamic ultrasound scattering method", The 23rd Workshop of Scattering Techniques, Tokyo, Nov. 11-12 (2011)

(f) Patents

2007

1) Q. Tran-Cong-Miyata, H. Nakanishi, M. Satoh, “Novel Fabrication Methods of Multiphase Polymeric Materials”, Japanese Patent Appl. No. 2007-191648 , assigned to Kyoto Institute of

Technology (Aug. 2007).

2) Q. Tran-Cong-Miyata, S. Ishino, H. Nakanishi, E. Ueda, "A Novel Fabrication Methods of Multiphase Polymeric Materials Using Computer-Assisted Irradiation Method", Japanese Patent Appl. No. 2007-238641 , assigned to Kyoto Institute of Technology (Aug. 2007).

2009

T. Norisuye, "Dynamic ultrasound scattering apparatus and the characterizing methods for microsphere suspensions", Japanese Patent Appl. No. 2009-114873 (2009), assigned to Kyoto Institute of Technology (2009).

g) Research Funds and Financial Supports

2007

1) Q. Tran-Cong-Miyata (Principal Investigator) and T. Norisuye, Grants-in-Aid for Scientific Research on Priority Area "Soft Matter Physics", Ministry of Education (MONKASHO), Japan No. 19031018, "Phase Separation Dynamics of Polymer Mixtures Temporally and Spatially Driven by Photochemical Reactions and Its Application to Materials Designing"

2) T. Norisuye, Grants-in-Aid for Young Scientists (Type B), Ministry of Education (MONKASHO), Japan No.18750190, "Studies on the bubble dynamics in viscoelastic polymer solutions by means of dynamics ultrasound scattering method".

3) T. Norisuye, Japan Regional Innovation Strategy program by the Excellence, 10-007, "Non-destructive analysis of soft matter by means of novel ultrasound techniques"

2008

1) Qui Tran-Cong-Miyata (Principal Investigator) and Tomohisa Norisuye, Grant-in-Aid for Scientific Research on Priority Area "Soft Matter Physics", Ministry of Education (MONKASHO), Japan No. 19031018, "Phase Separation Dynamics of Polymer Mixtures Temporally and Spatially Driven by Photochemical Reactions and Its Application to Materials Designing"

2) Qui Tran-Cong-Miyata, Grant-in-Aid for Scientific Research (Type B), Ministry of Education (MONKASHO), Japan No.20350107, "Novel Design of Multi-Components Polymers with Co-continuous Morphologies and Controlling Dispersion of Multi-walled Carbon Nanotubes".

3) T. Norisuye, Grants-in-Aid for Young Scientists (Type B), Ministry of Education (MONKASHO), Japan No. 20750178, "Novel techniques and its applications for microspheres by means of dynamics ultrasound scattering method".

2009

1) Qui Tran-Cong-Miyata (Principal Investigator) and Tomohisa Norisuye, Grant-in-Aid for Scientific Research on Priority Area "Soft Matter Physics", Ministry of Education (MONKASHO), Japan, No. 21015018, "Phase Separation Dynamics of Polymer Mixtures Temporally and Spatially Driven by Photochemical Reactions and Its Application to Materials Designing

2) Qui Tran-Cong-Miyata, Grant-in-Aid for Scientific Research (Type B), Ministry of Education (MONKASHO), Japan No.20350107, "Novel Design of Multi-Components Polymers with Co-continuous Morphologies and Controlling Dispersion of Multi-walled Carbon Nanotubes".

3) T. Norisuye, Grants-in-Aid for Young Scientists (Type B), Ministry of Education (MONKASHO), Japan No. 20750178, "Novel techniques and its applications for microspheres by means of dynamics ultrasound scattering method".

2010

1) Qui Tran-Cong-Miyata (Principal Investigator) and Tomohisa Norisuye, Grant-in-Aid for Scientific Research on Priority Area “Soft Matter Physics”, Ministry of Education (MONKASHO), Japan, No. 21015018, “Phase Separation Behavior of Polymer Mixtures Under Stationary Non-Uniform Experimental Conditions Driven by Computer-Assisted Irradiation Method”

2) Qui Tran-Cong-Miyata, Grant-in-Aid for Scientific Research (Type B), Ministry of Education (MONKASHO), Japan No.20350107, “Novel Design of Multi-Components Polymers with Co-continuous Morphologies and Controlling Dispersion of Multi-walled Carbon Nanotubes”.

3) T. Norisuye, Grants-in-Aid for Young Scientists (Type B) 22750205, "Dynamics Ultrasound Scattering analysis for sub micron particles in the presence of the acoustic radiation field".

2011

1) Q. Tran-Cong-Miyata, Grant-in-Aid for Scientific Research (Type C), Ministry of Education (MONKASHO), Japan No. 23550241, “Designing Polymer Materials with Programmable Surfaces Constructed by Spatially Graded Morphology Generated by Photochemical Reactions”

2) T. Norisuye, Grants-in-Aid for Young Scientists (Type B), Ministry of Education (MONKASHO), Japan, No. 22750205, "Dynamics Ultrasound Scattering analysis for sub micron particles in the presence of the acoustic radiation field".

Fibrous Material Science Laboratory
Takashi ITOH, Dr., Prof.
Susumu FUJIWARA, Dr., Associate Prof.
Masato HASHIMOTO, Dr., Assistant Prof.

I. Researches

Polymer crystals usually take imperfect structures because polymer chains are long enough. In general, the so-called crystalline polymers exhibit complex and hierarchical structures on the basis of such imperfect crystals. Polymer solids therefore form various higher-order structures and have a wide range of physical and chemical properties. In this laboratory, we systematically study the relationship between the structures of polymer solids and their physical properties by utilizing experimental methods, such as various electron microscopes, X-ray analysis, optical microscopes, optical scattering, infrared absorption, electric measurement, mechanical measurement, thermal analysis and computer simulation. The main research themes are as follows.

1. Phase transition in polymer crystals

Various experimental methods such as electron microscopes, X-ray analysis, infrared absorption, electric measurement, mechanical measurement and thermal analysis are used to study the reversible crystal phase transition and the irreversible crystal phase transition. We believe that the investigation of the mechanisms of such phase transitions will provide a hint to the development of new materials with desired properties.

2. Crystal growth of polymers

Various experimental methods such as optical microscopes and atomic force microscopes are used to study the effect of thermal history on polymer crystal growth from the melt, the microscopic growth mechanisms of single polymer crystals and the numerical quantification of polymer crystal morphologies through image processing. We also investigate the melt memory effect on polymer spherulites and mechanism of cavitation in the polymer melt (Figs.1 and 2).

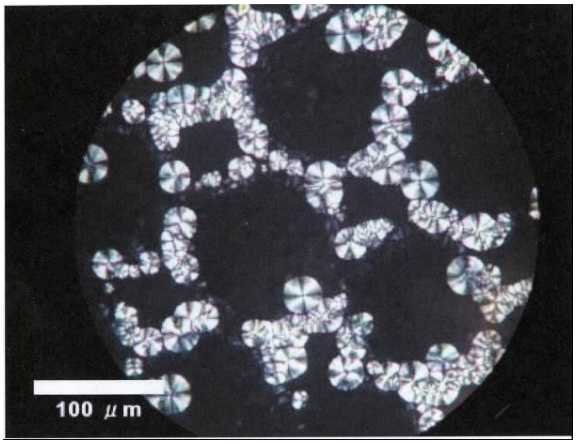

Fig.1. Cross-polarized optical micrograph of isotactic polystyrene spherulites in a sample partially sandwiching gold coating.

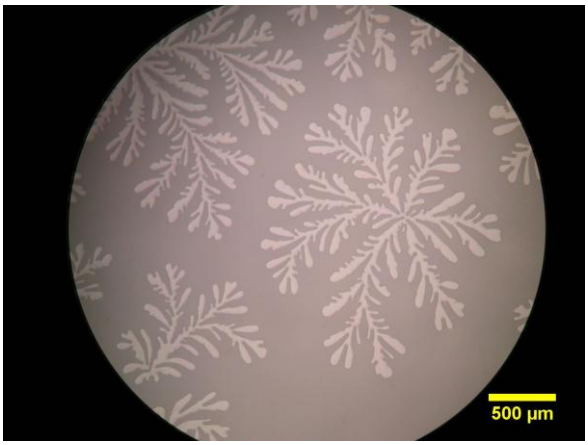

Fig.2. Optical micrograph of cavities with the viscous fingering in atactic polystyrene melt.

3. Structure formation of polymers and amphiphilic molecules

Computer simulations are carried out to study the structure formation of polymers and amphiphilic molecules. In particular, structure formations of an isolated single polymer chain (Fig. 3), isolated short chain molecules and a single polymer chain in solution as well as the spontaneous micelle formation and mesophase formation in amphiphilic solution (Fig. 4) are investigated. Moreover, we aim at exploring the universal self-organizing properties in nature through the clarification of the mechanisms of structure formation in soft matter systems such as polymeric and amphiphilic systems.

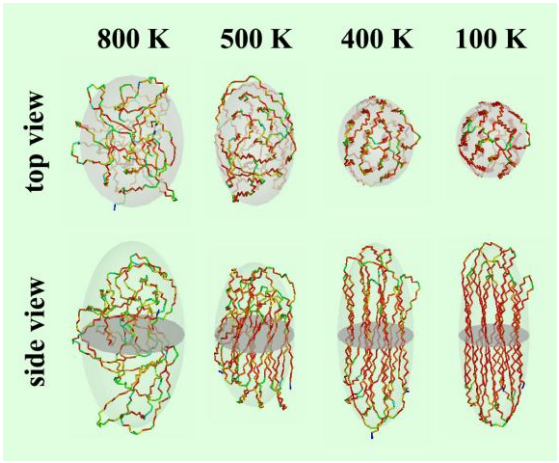

Fig.3. Computer simulation for structure formation of an isolated single polymer chain.

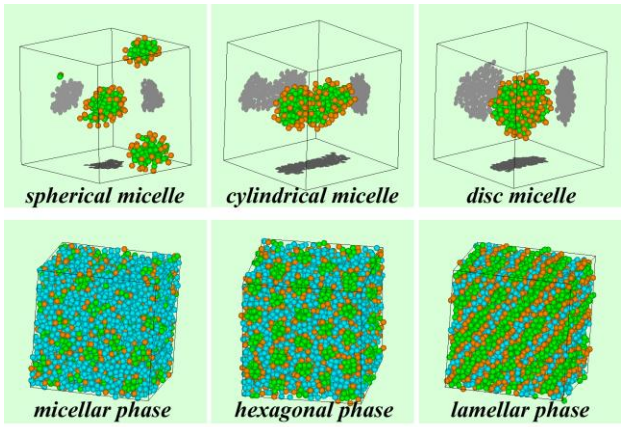

Fig.4. Computer simulation for spontaneous micelle formation and mesophase formation in amphiphilic solution.

II. Publications and Achievements

(a) Original papers

2007

1) Thuy-Trang Hua, T. Itoh, Jian-An HOU, S. Fujiwara and M. Hashimoto, "Freezing of High-Temperature Phase in Vinylidene Fluoride/Trifluoroethylene Copolymer Crystals on Vacuum-Evaporated Metal Surfaces", *Jpn. J. Appl. Phys.*, **46**, L1170-L1172 (2007).

2) Thuy-Trang Hua, T. Itoh, S. Fujiwara and M. Hashimoto, "Superlattice Epitaxy of Vinylidene Fluoride/Trifluoroethylene Copolymer Crystals on Highly Oriented Pyrolytic Graphite", *J. Phys. Soc. Jpn.* **76**, 124604 (2007).

3) H. Fukumura, S. Matsui, H. Harima, T. Takahashi, T. Itoh, K. Kisoda, M. Tamada, Y. Noguchi and M. Miyayama, "Observation of phonons in multiferroic BiFeO3 single crystals by Raman scattering", *J. Phys.: Condens. Matter*, **19**, 365224 (2007).

4) S. Fujiwara, T. Itoh, M. Hashimoto and Y. Tamura, "Molecular dynamics simulation of micelle formation in amphiphilic solution", *Mol. Simul.* **33**, 115-119 (2007).

2009

1) Y. Okubo, S. Mori, K. Yamamoto, D. Hamada, H. Kohno, K. Fujiwara, M. Hashimoto, K. Ikeuchi and N. Tomita, "Mechanical Interaction between Vitamin E-Containing Ultrahigh Molecular

Weight Polyethylene and Co-28Cr-6Mo Alloy in Water", *J. Biomech. Sci. Eng.* **4**, 166-173 (2009).

2) S. Fujiwara, M. Hashimoto and T. Itoh, "Molecular Dynamics Simulations for Structure Formation of Polymers and Self-Assembly of Amphiphilic Molecules (in Japanese)", *Kobunshi Ronbunshu* **66**, 396-405 (2009).

3) T. Takahashi, T. Itoh, S. Fujiwara and M. Hashimoto, "Novel Primary Dispersion in Viscoelastic Behavior of Ferroelectric Nylon 6", *Polymer J.* **41**, 354-355 (2009).

4) S. Fujiwara, T. Itoh, M. Hashimoto and R. Horiuchi, "Molecular dynamics simulation of amphiphilic molecules in solution: Micelle formation and dynamic coexistence", *J. Chem. Phys.* **130**, 144901 (2009).

2010

1) H. Nakamura, A. Ito, S. Saito, Y. Tamura, S. Fujiwara, N. Ohno and S. Kajita, "Comparison with Surfaces of Diamond and Graphite for Adsorption of Hydrogen Solution", *Plasma Fusion Res.* **5**, S2072 (2010).

2) Y. Tamura, S. Fujiwara and H. Nakamura, "Haptization of molecular dynamics simulation with thermal display", *Plasma Fusion Res.* **5**, S2107 (2010).

3) S. Fujiwara, T. Itoh, M. Hashimoto, H. Nakamura and Y. Tamura, "Effect of Molecular Rigidity on Micelle Formation in Amphiphilic Solution", *Plasma Fusion Res.* **5**, S2114 (2010).

4) K. Sogo, Y. Kishikawa, S. Ohnishi, T. Yamamoto, S. Fujiwara and K. M. Aoki, "Correlated Anomalous Diffusion - Random walk and Langevin equation -", *J. Math. Phys.* **51**, 033302 (2010).

2011

1) M. Segawa, H. Kuromitsu and T. Itoh, "Change in Surface Morphology of Polyvinyl Chloride Extracorporeal Circulation Pump Tube Caused by Roller-pump Stress (in Japanese)", *Transactions of Japanese Society for Medical and Biological Engineering*, **49**, 544-550 (2011).

2) R. Shirasaki, Y. Yoshikai, H. J. Qian, S. Fujiwara, Y. Tamura and H. Nakamura, "Dissipative Particle Dynamics Simulation of Phase Behavior in Bolaamphiphilic Solution", *Plasma Fusion Res.* **6**, 2401116 (2011).

3) Y. Tamura, K. Ukita, N. Mizuguchi and S. Fujiwara, "Design Support System with Haptic Feedback and Real-Time Interference Function", *Plasma Fusion Res.* **6**, 2406061 (2011).

4) S. Fujiwara, T. Itoh, M. Hashimoto, Y. Tamura, H. Nakamura and R. Horiuchi, "Molecular Dynamics Simulation of Micellar Shape Change in Amphiphilic Solution", *Plasma Fusion Res.* **6**, 2401040 (2011).

5) Y. Tamura, S. Fujiwara, T. Umetani and H. Nakamura, "Bracelet shaped thermal display for representing numerical data", *J. Electron. Mater.* **40**, 823-829 (2011).

6) S. Fujiwara, D. Funaoka, T. Itoh and M. Hashimoto, "Molecular dynamics simulation for phase behavior of amphiphilic solution", *Comput. Phys. Commun.* **182**, 192-194 (2011).

(b) Books

2008

S. Fujiwara, in "At Home in the Universe (in Japanese)", pp. 191-371, (translation of "At Home in

the Universe" written by S. Kauffman), Chikuma Shobo (2008).

(c) Reviews and Reports

2007

S. Fujiwara, M. Hashimoto, T. Itoh and Y. Tamura, "Molecular Dynamics Simulation of Micelle Formation in Amphiphilic Solution: Identification of Micellar Shape", Annual Report of National Institute for Fusion Science, April 2006 - March 2007, p. 367 (2007).

2008

1) S. Fujiwara, M. Hashimoto, T. Itoh and R. Horiuchi, "Molecular Dynamics Simulation of Amphiphilic Molecules in Solution: Mesophase Formation", Annual Report of National Institute for Fusion Science, April 2007 - March 2008, p. 359 (2008).
2) S. Fujiwara, "Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves (in Japanese)", (book review) *BUTSURI* **63**, 965-966 (2008).

2009

S. Fujiwara, M. Hashimoto, T. Itoh and R. Horiuchi, "Molecular Dynamics Simulation of Micelle Formation in Amphiphilic solution: Dynamic Coexistence of Micellar Shapes", Annual Report of National Institute for Fusion Science, April 2008 - March 2009, p. 319 (2009).

2010

1) S. Fujiwara, T. Itoh, M. Hashimoto, H. Nakamura, R. Horiuchi and Y. Tamura, "Dynamics Simulation of Micelle Formation in Amphiphilic solution: Effect of Molecular Rigidity", Annual Report of National Institute for Fusion Science, April 2009 - March 2010, p. 346 (2010).
2) S. Fujiwara, "Large-Scale Molecular Simulation of Higher-Order Structure Formation by Amphiphilic Molecules", Activity Report 2009, Supercomputer Center, MDCL ISSP University of Tokyo, p. 211 (2010).

2011

1) S. Fujiwara, T. Itoh, M. Hashimoto, H. Nakamura, R. Horiuchi and Y. Tamura, "Molecular Dynamics Simulation of Micellar Shape Change in Amphiphilic Solution: Effect of Molecular Rigidity", Annual Report of National Institute for Fusion Science, April 2010 - March 2011, p. 389 (2011).
2) S. Fujiwara, R. Maruyama, T. Itoh, M. Hashimoto and R. Horiuchi, "Molecular Dynamics Simulation of Melting Process in *n*-Nonane Ultrathin Films", Annual Report of National Institute for Fusion Science, April 2010 - March 2011, p. 390 (2011).
3) S. Fujiwara, "Molecular Simulation of Higher-Order Structure Formation by Amphiphilic Molecules", Activity Report 2010, Supercomputer Center, MDCL ISSP University of Tokyo, p. 203 (2011).

(d) Awards

(e) Invited Lectures

2007

S. Fujiwara, "Structure and Formation Dynamics of Polymer Crystals (in Japanese)", 12th Annual Meeting of the Research Group on Computational Polymer Science, The Society of Polymer Science, Japan (2007).

2008

1) S. Fujiwara, "Molecular Dynamics Simulation of Ordering Processes in Polymer Systems (in Japanese)", Joint Symposium of the fieds 9 and 12, 2008 Autumn Meeting of the Physical Society of Japan (2008).
2) S. Fujiwara, "Molecular Dynamics Simulations for Structure Formation of Polymers and Self-Assembly of Amphiphilic Molecules (in Japanese)", 2nd Public Symposium of the Grant-in-Aid for Scientific Research on Priority Area "Soft Matter Physics" (No. 463) 2006-2010, Ministry of Education, Culture, Sports, Science and Technology of Japan (2008).

2011

S. Fujiwara, "Molecular Dynamics Study on Structure Formation of Polymers and Self-Assembly of Amphiphilic Molecules (in Japanese)", Joint Seminar of the Theoretical Groups, Tokyo University of Pharmacy and Life Sciences (2011).

(f) Patents

(g) Funds and Financial Supports

2007

S. Fujiwara, Grant-in-Aid for Scientific Research on Priority Area "Soft Matter Physics", Public Participation Research 19031019, "Theoretical and Simulational Study of Soft Matter Interfaces".

2008

S. Fujiwara, Grant-in-Aid for Scientific Research on Priority Area "Soft Matter Physics", Public Participation Research 19031019, "Theoretical and Simulational Study of Soft Matter Interfaces".

2010

S. Fujiwara, Grant-in-Aid for Scientific Research, Scientific Research (C) 22540419, "Investigation of the Mechanisms of Surface Melting and Surface Freezing of *n*-Alkane Uultrathin Films by Large-Scale Molecular Simulation".

2011

1) T. Itoh, Research Grant, Mitsuboshi Belting Ltd.
2) S. Fujiwara, Grant-in-Aid for Scientific Research, Scientific Research (C) 22540419, "Investigation of the Mechanisms of Surface Melting and Surface Freezing of *n*-Alkane Uultrathin Films by Large-Scale Molecular Simulation".

Polymer Mechanics Laboratory
Masaoki TAKAHASHI, Dr., Prof.
Yukihiro NISHIKAWA, Dr., Associate Prof.

I. Researches

1. Structure-Rheology Relationships

The objectives of this field of research are:

1) To clarify relationships between structure and rheology in polymer alloys and blends, and
2) To clarify relationships among structure, rheology and functionality in polymer composites.

The following investigations have been made for each objective.

1) Relationships between structure and viscoelasticity in immiscible polymer blends

Experimental observation of droplet-phase deformation was made under external step-shear strains, and shape recovery of the droplet due to the interfacial tension was analyzed. The *interface tensor*, or the anisotropy of interface under the strain, was calculated from the observed droplet shape (*flat ellipsoid, rod-like, dumbbell and spheroid*). Based on the Doi-Ohta theory, this calculation of the interface tensor enabled us to predict the *stress tensor* for the deformed interface. The predicted stress agreed with experimental data fairly well for polymer blends with small and large interfacial tensions and with narrow and broad distribution of droplet size. This way of predicting the stress tensor from the observed shape of interface has been extended to polymer blends with bicontinuous (co-continuous) structure. 3D images of deformed interface of bicontinuous structure have been observed, utilizing a high-contrast X-ray CT developed by Nishikawa et al. The interface and stress tensors are now in the process of calculation from the observed 3D images.

In the Doi-Ohta theory, only the *Laplace pressure term* was considered and the *interface velocity term* was neglected in calculating the stress tensor for the interface. We calculated the interface velocity term in the step-strain test and evaluated the effect of the term. Inclusion of this term resulted in better agreement of the prediction with experimental data in the final stage of stress relaxation.

From observation of two deformed droplets at a short distance, we found coalescence of the droplets under large step shear strains. Hydrodynamic interactions between deformed droplets were analyzed and the coalescence was explained from the predicted matrix flows between and around the droplets.

2) Relationships among structure, viscoelasticity and functionality in polymer (blend) composites

When fillers are mixed into binary polymer blend melts, the fillers are localized in one phase of the polymer blend. We found that nanocarbons are localized in a polymer phase with lower *interfacial energy* between nanocarbon and polymer component. There are a few exceptions for polymer blends with very different *chain-flexibility*. Flexible polymers such as high density polyethylene and polypropylene can adsorb onto rough surfaces of carbon black and rough ends of carbon nanofibers (VGCFs) without great loss of entropy (entropy penalty). Polymer blends with bicontinuous structure were found to be good templates for network formation of *nanocarbons*, *zirconia*, *alumina* and *silver particles*. In immiscible polymer blends, bicontinuous structure usually appears when i) the interfacial tension between polymer components is small, ii) the viscosity of the components is comparable and

iii) the composition is around 50:50. By utilizing the bicontinuous structure as a template for percolation network, the critical fraction of filler for percolation can be reduced to half (or smaller than that in a favorable case), compared with the fraction in a composite with a single polymer matrix (either component). Network formation of fillers results in appearance of plateau region in the storage modulus at low frequencies. In case of conductive fillers, network formation enhances electrical and/or thermal conductivity. Localization of nanocarbons at the interface of bicontinuous structure will be an ultimate technique to enhance the electrical conductivity, and this method is under investigation.

2. 3D Microscopy and 3D Image Analyses

In order to understand the relationship between the mechanical properties and the structures in polymeric systems, the structural analysis is the other end of the research field as well as the rheological studies. For this purpose, we propose the concept of three-dimensional (3D) microscopy (3D-scopy). In 3D-scopy, the 3D image of the microscopic structure of the material is obtained by somehow, such as confocal microscopy, transmission electron microtomography, and X-ray computerized tomography (CT), and then the 3D image is subjected to the 3D image analysis. Since the 3D image includes all structural aspects in a given spatial resolution, 3D-scopy can be an ultimate structural analysis method. Recently, we concentrate ourselves to the researches on X-ray CT. X-ray CT has been considered to be inappropriate in polymer science since most of polymers are transparent to X-rays. However, we developed a high-contrast X-ray CT and concluded that X-ray CT has a sufficient contrast-performance to resolve the difference of the polymer species. Now X-ray CT is an emerging research tool in polymer science. Studies on X-ray CT consist of the development and the application of X-ray CT.

Development of X-ray CT includes the theoretical study of reconstruction method, developing the reconstruction software, the technical design of the X-ray CT hardware, and studies on the sample preparations. As the theoretical study, we proposed a novel reconstruction technique based on Monte Carlo method, which is completely different from the standard reconstruction method, filtered back-projection (FBP), and has a lot of advantages to FBP. We also develop new X-ray CT apparatuses in collaboration with several companies in order to achieve high spatial resolutions.

Thus developed X-ray CT is applied to many polymer systems, such as, the binary and ternary polymer blends, the glass-fiber or carbon-fiber or cellulose-fiber composites, the form materials, and so on. The X-ray CT is applicable to the opaque samples which is one of the big advantages of X-ray CT in comparison to light scattering and confocal microscopy. Typical applications are PS/PMMA blends and composites. Polymer foams are also an important topic for X-ray CT. The buckling of the foam cells under compression was three-dimensionally observed by X-ray CT for the first time. The phase-separation structures in ternary polymer blends were systematically surveyed by X-ray CT, and a lot of new morphologies were discovered.

Generally, 3D-scopy provides the 3D images of the objects. The analysis of the 3D images is also important research field. At this moment, we can perform network analysis, particle analysis, distance analysis, and orientation analysis in 3D. Other analysis techniques are still under investigation.

II. Publications and Achievements

(a) Original papers

2007

1) M. Takahashi, P. H. P. Macaubas, K. Okamoto, H. Jinnai and Y. Nishikawa, "Stress Prediction for Polymer Blends with Various Shapes of Droplet Phase", *Polymer*, **48**, 2371-2379 (2007).
2) M. Takahashi, S. Osawa, H. Jinnai, H. Yamane and H. Shiomi, "Dispersion State of Zirconium Oxide Particles in Polymer Blends and Viscoelastic Behavior of the Composites", *J. Soc. Rheology, Japan*, **35**, 1-9 (2007).
3) P. H. P. Macaubas, H. Kawamoto, M. Takahashi, K. Okamoto, and T. Takigawa, "Shape and Structure Recovery of an LCP Droplet under a Large Step Strain: Observation and Stress Calculation", *Rheol. Acta*, **46**, 921-932 (2007).
4) M. Takahashi and K. Okamoto, "Retraction of Rod-like and Spheroidal Droplets and Stress Relaxation after Step Shear Strain in Polymer Blends", *J. Soc. Rheology, Japan*, **35**, 199-205 (2007).
5) M. Takahashi, "Study on Structure-Rheology Relationships in Multiphase Polymeric Systems", *J. Soc. Rheology, Japan*, **35**, 235-244 (2007).
6) T. Hashimoto, Y. Nishikawa, K. Tsutsumi, "Identification of the Voided Double-Gyroid-Channel: A New Morphology in Block Copolymers", *Macromolecules*, **40**, 1066-1072 (2007).
7) S. Koizumi, Y. Yamane, S. Kuroki, I. Ando, Y. Nishikawa, H. Jinnai, "Three-dimensional Observation of Phase-separated Poly(methyl methacrylate)/Poly(styrene-ran-4-bromostyrene) Blends by 3D NMR Microscopy with X-ray Microscopy", *J. Appl. Polym. Sci.*, **103**(1), 470-475 (2007).
8) H. Saito, K. Kanamori, K. Nakanishi, K. Hirao, Y. Nishikawa, H. Jinnai, "Three-dimensional Observation of Macroporous Silica Gels and the Study on Structural Formation Mechanism", *Colloid. Surface A*, **300**, 245-252 (2007).

2008

1) K. Okamoto and M. Takahashi, "Effects of Interface Velocity on the Stress Tensor in Immiscible Polymer Blends: Retraction of Spheroidal Droplets and Stress Relaxation", *J. Soc. Rheology, Japan*, **36**, 43-49 (2008).
2) K. Okamoto, K. Iwase, M. Ishikawa, M. Takahashi, "Effects of Droplet Size and Volume Fraction on Relaxation Modulus of Immiscible Polymer Blends: Inclusion of Interface Velocity Term", *J. Soc. Rheology, Japan*, **36**, 117-123 (2008).
3) K. Okamoto S. Iwatsuki, M. Ishikawa and M. Takahashi, "Hydrodynamic Interaction and Coalescence of Two Droplets under Large Step Shear Strains", *Polymer*, **49**, 2014-2017 (2008).
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2009

K. Okamoto, M. Yamaguchi, M. Takahashi, "Hydrodynamic Interaction Model for two Droplets

under Large step Shear Strains", *J. Soc. Rheology, Japan*, **37**, 121-128 (2009).

2011

1) Y. Nishikawa, N. Ohta, Y. Komasu, M. Takahashi, "Application of High-contrast X-ray Computerized Tomography to Carbon Fiber/Polymer Composites (in Japanese)", *J. Soc. Mat. Sci., Japan*, **60**(1), 29-34 (2011).
2) Y. Nishikawa, S. Baba, M. Takahashi, "Optimization of X-ray Computerized Tomography for Polymer Materials", *Intl. J. Polym. Mat.*, in press.

(b) Books

2011

Y. Nishikawa and M. Takahashi, "Observation of Polymer Materials by using X-ray Computerized Tomography (in Japanese)" in "Pastics Age Encyclopedia shinpo-hen 2012" pp. 105-110, Plastics Age Co. Ltd. (2011).

(c) Reviews and Reports

2007

M. Takahashi, H. Okumura, J. Matsubayashi, Y. Nishikawa, "Flow Induced Orientation of Microphase Separated Structure and Rheology in Block Copolymers (in Japanese)", Annual Report of the Research Institute for Chemical Fibers, Japan, **64**, 77-86 (2007).

2008

1) M. Takahashi, "Structure and Rheology of Multiphase Polymeric Systems (in Japanese)", *Chemical Engineering*, **53**, 24-29 (2008).
2) M. Takahashi, "Progress in 10 years: Fundamental Properties of Polymer Melts (in Japanese)", *J. Japan Society of Polymer Processing* (*Seikei Kakou*), **20**, 527-532 (2008).
3) M. Takahashi, K. Kimura, T. Sudo and S. Osawa, "Dispersion Control of Particles Utilizing Phase Separated Structure of Polymer Blends (in Japanese)", Annual Report of the Research Institute for Chemical Fibers, Japan, **65**, 66-72 (2008).

2009

M. Takahashi, K. Okamoto and P. H. P. Macaubas, "Prediction of Stress Tensor Resulting from Deformed Interface in Polymer Blends and Comparison with Experimental Data (in Japanese)", Annual Report of the Research Institute for Chemical Fibers, Japan, **66**, 75-81 (2009).

2010

1) M. Takahashi, Y. Nishikawa, N. Mukai, R. Ishikawa and K. Kimura, "High-performing Electromagnetic-Wave Absorber: Network Formation of Nanocarbons Utilizing Selective Adsorption of Polymer Chains and Phase Separated Structure (in Japanese)", Annual Report of the Research Institute for Chemical Fibers, Japan, **67**, 78-85 (2010).
2) Y. Nishikawa and M. Takahashi, "Electrical Conductivity, Mechanical Property, and Structure in Carbon Nano-fiber/Polymer Composites (in Japanese)", *Chemical Engineering*, **55**(9), 665-669 (2010).

2011

1) M. Takahashi and Y. Nishikawa, "3D Structure Observation by X-ray CT (in Japanese)", *J. Adhesion Soc. Japan* (*Adhesion*), **47**(11), 453-459 (2011).
2) M. Takahashi, Y. Nishikawa, H. Hatakeyama and H. Taniyama, "3D Structure Observation by X-ray CT and Rheology for Polymer Blends with Bicontinuous Structure (in Japanese)", Annual Report of the Research Institute for Chemical Fibers, Japan, **68**, 77-84 (2011).

(d) Awards

2007

M. Takahashi, The SRJ Award (The Society of Rheology, Japan), "Study on Structure-Rheology Relationships in Multiphase Polymeric Systems".

(e) Invited Lectures

2007

M. Takahashi, "Study on Structure-Rheology Relationships in Multiphase Polymeric Systems (Award Lecture)", 34th Annual Meeting of the Society of Rheology, Japan (2007).

2010

M. Takahashi, "Viscoelasticity of Copolymers and Polymer Blends with Bicontinuous and Other Structures", ISSP International Workshop on Soft Matter Physics, University of Tokyo, Aug. 9-13 (2010)

(f) Patents

2011

1) Y. Nishikawa, "Image Reconstruction Method, Image Reconstruction Apparatus, Image Reconstruction Program, Computerized Tomography Apparatus", US Patent No. 8090182.
2) Y. Nishikawa, "Image Reconstruction Method, Image Reconstruction Apparatus, Image Reconstruction Program, Computerized Tomography Apparatus", Chinese Patent No. ZL200780038491.7.
3) T. Kishi, Y. Nishikawa, "Image Reconstruction Method and Image Reconstruction Apparatus", Japanese Patent Publication No. 2010-99535.
4) T. Kishi, Y. Nishikawa, "Image Reconstruction Method and Image Reconstruction Apparatus", Japanese Patent Appl. No. 2011-088493.

(g) Funds and Financial Supports

2007

M. Takahashi, Grant-in-Aid for Scientific Research, Scientific Research (B) 18350119, "Invention of Electromagnetic-wave Absorbing Composites Utilizing Bicontinuous Polymer Structure and Percolation of Nano-carbons".

2009

1) Y. Nishikawa, Grant-in-Aid for Challenging Exploratory Research (B) 21750219, “Development of Spindle Method for X-ray Computerized Tomography with Nanometer-scale Spatial Resolution.”
2) S. Baba, Y. Nishikawa, JST Chiiki-niizu Sokuougata, “Development of X-ray Computerized Tomography for Electric Devices.”

2010

1) M. Saigan, Y. Nishikawa, JST A-STEP Feasibility Study AS2211139F, “Metal Artifact Reduction of Dental X-ray Computerized Tomography.”
2) M. Takahashi, KIT-KANEKA Comprehensive Cooperation Research Project (2010-2011).

Textile Engineering Design Laboratory
Ryuichi AKIYAMA, Dr., Prof.
Katsufumi TANAKA, Dr., Associate Prof.
Haruki KOBAYASHI, Dr., Assistant Prof.

I. Researches

- Physical Properties of Liquid Crystals (Figs.1, 2)
- Sensory Test for Textile Products (Fig.3)
- The Electro-Rheological Effect of Nano- Suspensions (Figs.4, 5)
- Structure and Physical Properties of Liquid Crystalline Polymers, Nano-Particles and Nano-Fibers in Polymers
- Mechanical Properties of Nanofiller-Dispersed Materials (Figs.6, 7)

Physical Properties of Liquid Crystals and Sensory Test for Textile Products

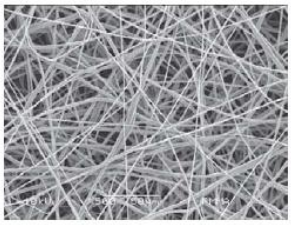

Fig.1 SEM micrograph of a mat of nano-fibers

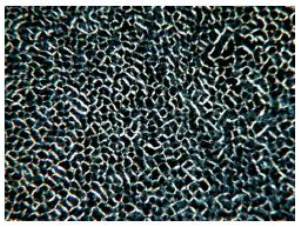

Fig.2 Polarized optical micrograph of a particle network developed from a mixture of 8CB/HEMA after UV curing.

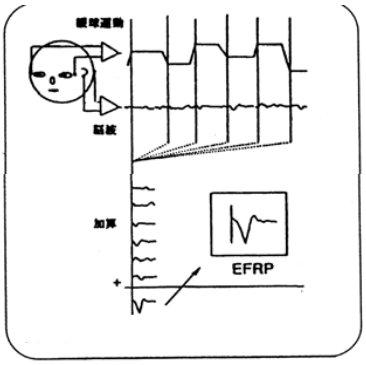

Fig.3 Sensory Test for Textile Products.

The Electro-Rheological Effect of Nano- Suspensions

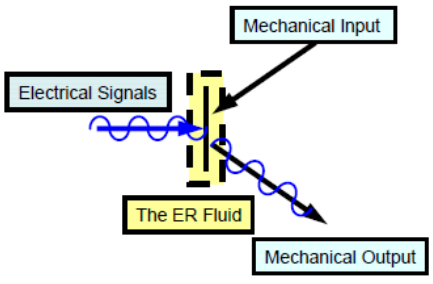

Fig.4 The ER effect

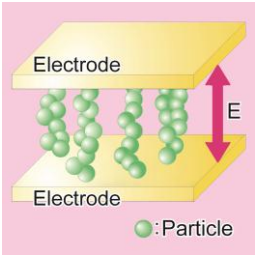

Fig.5 A chain-like microstructure under an electric field.

The electro-rheological effect (the ER effect) is the reversible rheological responses of fluids only by application and removal of an external electric field. **The mechanical output** can be controlled simply by desirable information as **electrical signals** superposed upon the electric field (Fig.4). **The nano-suspension** composed of polarizable nano-particles and insulating oil is known to show the ER **effect**. Microstructures such as chain-like one or ring-like one are closely related to the ER effect (Fig.5). The physical properties of such ER nano-susupensions and composites are studied in relation to the microstructures developed under electric and/or shear fields.

Mechanical Properties of Nanofiller-Dispersed Materials

Objective:

Our goal is to improve mechanical properties of polymer materials by adding nano-fillers.

Approach:

- To quantify the mechanical properties, various types of mechanical tests (tensile, bending, compressive, fracture toughness, fatigue, wear, and so on) are being conducted.
- Statistical analyses are being performed on the data of mechanical tests.
- Morphological changes are being assessed using x-ray techniques and optical and electrical microscopies.

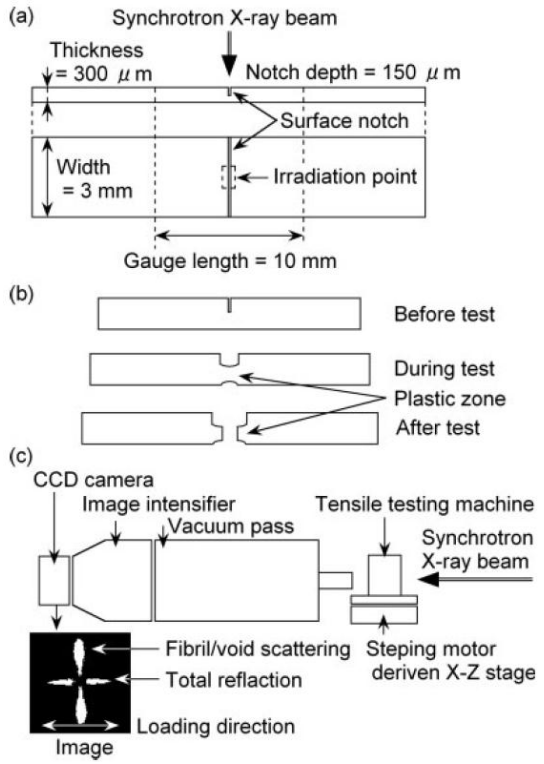

Fig. 6 Schematic illustrations of surface-notched specimen for SAXS measurements (a), changes of shape of specimen during tensile deformation (b), and geometry of time-resolved SAXS measurements during tensile deformation (c).

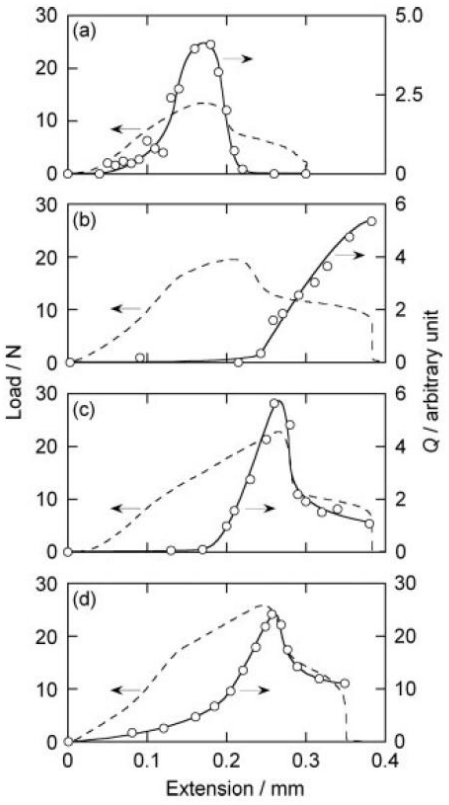

Fig. 7 Integrated intensity Q (circle) and load of film (broken line) versus extension of film for neat PET film (a), CB (2 wt %)/PET composite film (b), MWCNT-I (1 wt %)/PET composite film (c) and MWCNT-II (2 wt %)/PET composite film (d).

(Figures 6 and 7 are cited from *J. Appl. Polym. Sci.*, **106**, 152-160 (2007).)

II. Publications and Achievements

(a) Original papers

2007

1) K. Tanaka, T. Morina, Y. Tanabe, and R. Akiyama, "Concentration dependences of dielectric properties at 10^5 Hz and 10^6 Hz for aqueous solutions of hydroxypropyl cellulose", *Liq. Cryst.*, **34**, 1019-1028 (2007).
2) K. Tanaka, H. Nakahori, K. Katayama, and R. Akiyama, "Linear viscoelastic properties of electro-rheological nano-suspension confined to narrow gap between electrodes", *Colloid Polym. Sci.*, **285**, 1201-1211 (2007).
3) H. Kobayashi, M. Shioya, T. Tanaka, T. Irisawa, S. Sakurai and K. Yamamoto, "A Comparative Study of Fracture Behavior between Carbon Black/PET and Multi-Walled Carbon Nanotube/PET Composite Films", *J. Appl. Polym. Sci.*, **106**, 152-160 (2007).
4) H. Kobayashi, M. Shioya, T. Tanaka and T. Irisawa., "Synchrotron Radiation Small-angle X-ray Scattering Study on Fracture Process of Carbon Nanotube/Poly(ethylene terephthalate) Composite Films", *Comp. Sci. Tech.*, **67**, 3209-3218, (2007).
5) H. Kobayashi, M. Shioya, J. Yamashita and T. Hirano, "Formation Mechanism of Pores Contained in PVDF-based Carbon Films Derived through Chemical and High-temperature Heat-treatments", *Sen-i Gakkaishi*, **63**, 152-158, (2007).

2008

1) K. Tanaka, Y. Tanabe, T. Morina, and R. Akiyama, "*In-situ* monitoring of a film preparation process for hydroxypropyl cellulose cast from isotropic aqueous solution using microdielectrometry", *Liq. Cryst*., **35**, 253–264 (2008).
2) K. Tanaka, Y. Tanabe, and R. Akiyama, "Microdielectrometric monitoring of film preparation process with oriented domains for hydroxypropyl cellulose cast from isotropic aqueous solution under the sinusoidal electric field with large amplitude", *Liq. Cryst.*, **35**, 937-951 (2008).
3) K. Kitano, M. Chino, K. Tanaka, and R. Akiyama, "Electro-optical properties of liquid crystal – Polyacrylonitrile fiber composites", *Liq. Cryst.*, **35**, 1225-1235 (2008).

2009

1) K. Tanaka, N. Sezaki, H. Nakahori, and R. Akiyama, "Apparent yield stresses and microstructures of electro-rheological nano-suspensions under no external electric fields", *Nihon Reoroji Gakkaishi*, **37**, 17-23 (2009).
2) S. Kutsumizu,, K. Hosoyama, M. Yamada, K. Tanaka, R. Akiyama, S. Sakurai, and E. Funai, "Smectic C to cubic phase transition of 4'-n-docosyloxy-3'-nitrobiphenyl- 4-carboxylic acid (ANBC-22) and AC electric field effect", *J. Phys. Chem. B*, **113**, 640-646 (2009).
3) K. Fujihira, T. Irisawa, H. Kobayashi and M. Shioya, "Specimen geometry dependent effects of vapor grown carbon fibers on fracture toughness of polyamide 6", *International Journal of Polymer and Technologies*, **1**, 35-41, (2009).

2010

1) K. Tanaka, N. Nakagawa, and R. Akiyama, "Flow behavior and microstructure developed between

parallel plate electrodes for electro-rheological nano-suspensions under no external electric fields", *Nihon Reoroji Gakkaishi*, **38**, 93-97 (2010).

2) T. Irisawa, H. Kobayashi, K. Fujihira, M. Shioya and J. Kaneko, "A method to determine wear rates of fibers and its application to polymeric fibers added with inorganic fillers", *Wear*, **268**, 1148-1156, (2010).

2011

1) K. Tanaka, T. Hira, R. Fukui, N. Nakagawa, R. Akiyama, M. Nakano, K. Yoshida and T. Tsujita, "Development and flow evaluation of electro-rheological nano-suspensions", *Colloid. Polym. Sci.*, **289**, 855-862 (2011).

2) K. Tanaka, T. Araki, T. Nozaki, R. Tanaka, H. Kobayashi and R. Akiyama, "The effects of carbon nano-fibre on the liquid crystalline behaviour and cholesteric pitch of aqueous solutions of hydroxypropyl cellulose", *Liq. Cryst*, in press.

(b) Books

(c) Reviews and Reports

2007

M. Shioya, H. Kobayashi, T. Tanaka, T. Irisawa, S. Sakurai and K. Yamamoto, "Detection of crazes in CNT/PET composites under tensile deformation", *Photon Factory Activity Report, (High Energy Accelerator Research Organization (KEK), Institute of Materials Structure Science (IMSS))*, **24 (B)**, 148 (2007)..

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M. Shioya, H. Kobayashi, T. Irisawa, T. Suei, K. Fujihira, S. Sakurai and K. Yamamoto, "Fracture toughness of PET fibers, PET films and CNT/PET composite films", *Photon Factory Activity Report, (High Energy Accelerator Research Organization (KEK), Institute of Materials Structure Science (IMSS))*, **25(B)**, 118 (2008).

2009

K. Tanaka, and R. Akiyama, "Electrically induced microstructures in micro- and nano-suspensions and related physical properties", *Polym. J.*, **41**, 1019-1026 (2009).

2010

K. Tanaka, and R. Akiyama, "Preparation and Electrical Orientation for Cast Films via Liquid Crystalline Phase (in Japanese)", *Ekisyo* (Liquid Crystals), **14**, 169-174 (2010).

(d) Awards

2008

H. Kobayashi, The Paper Award (The Society of Fiber Science and Technology, Japan), "Formation Mechanism of Pores Contained in PVDF-based Carbon Films Derived through Chemical and High-temperature Heat-treatments".

(e) Invited Lectures

2007

1) K. Tanaka, Y. Tanabe, and R. Akiyama, “Yield behavior of electro-rheological nano- and micro-suspensions, and their microstructures”, The 27th regular meeting of Division of Electro-Rheology, The Society of Rheology, Japan, (2007).
2) K. Tanaka, Y. Tanabe, and R. Akiyama, “Film preparation of liquid crystalline polymers under electric fields”, Tokai Branch, The Society of Fiber Science, Japan, (2007).

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(f) Patents

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3) Y. Nakatsuka, S. Kiyohara, M. Tan, K. Ikeda, K. Tanaka, R. Akiyama, "Dispersion and redispersion methods for dispersoids as well as crush method for aggregated dispersoids, and devices thereof", Eur. Pat. Appl. (2007), EP 1870156 A1 20071226.
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T. Hiraku, M. Okada, Y. Nakamura, K. Tanaka, “Microchip and bubble-separation method thereof”, Japanese Patent No. 4646125.

(g) Funds and Financial Supports

2007

1) K. Tanaka (a member of researchers), Project for Creation of Fiber Science and Technology for the 21st Century – Development of Neo-Fiber Technology, MEXT University R& D Expenditure. (2007-2011).

2) K. Tanaka, KIT-NITTO Comprehensive Cooperation Research Project (2007-2008).

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K. Tanaka, The Cooperative Research Program of the Institute of Fluid Science, Tohoku University (2009-2011).

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K. Tanaka, KIT-KANEKA Comprehensive Cooperation Research Project (2010-2011).

Condensed Matter Physics Laboratory
Yasuo SARUYAMA, Dr., Prof.
Haruhiko YAO, Dr., Associate Prof.

I. Researches

Research interests of this laboratory include phase diagram and transition of state of soft matters such as polymers, liquid crystals, lipids, biomaterials. Further attention is paid to slow dynamics of the soft matters. Since the soft matters are composed of molecules with complex structures, they exhibit various types of molecular packing from the three dimensionally ordered crystals to the glasses without long range order depending on temperature, pressure, mixing ratio, concentration of the solution and so on. It is notable that the macroscopic properties such as heat capacity, density, relaxation time, degree of birefringence etc. depend on the history of the material significantly. In the soft matters large amplitude molecular motions, for example change in the molecular shape and exchange of the molecular positions, play important roles on the material properties. These molecular motions are highly cooperative and their correlation times are often very long as typically observed in the glass transition. The soft matters are useful as functional materials because of the wide variety of the molecular packing, the flexible macroscopic properties and the characteristic slow dynamics. In order to optimize the material functions it is important to understand the origins of the structures, the properties and the dynamics.

In the research of this laboratory much effort is made for development of original instruments for highly accurate experiments. Various instruments with much higher performance than commercial instruments have been developed in this laboratory. New concepts and models for the phenomena and the properties are proposed based on the reliable experimental data. Some instruments are introduced below.

1. High sensitivity differential scanning calorimeter (DSC).

The sensitivity of this DSC is as one thousand times as that of commercial instruments. This DSC has been applied to measurement of heat capacity of human stratum corneum and construction of the phase diagram of mixed systems of lipids and cholesterol. The former was carried out with one sheet (ca. 10μm) of the sample to avoid artifacts due to stacking of thin samples. The heat of transition of the latter was very small and could not be detected with a commercial instrument.

2. An instrument for temperature modulated dielectric measurement.

This instrument was developed to study the kinetics of the *response of the relaxation time to quick temperature change* around the glass transition of polymers. This *relaxation of dynamics* is a new type of relaxation proposed and confirmed firstly in the world.

3. Ultra high pressure ac calorimeter.

This instrument enables highly accurate calorimetry under 1GPa hydrostatic pressure. It has been applied to solid state phase transitions of polytetrafluoroethylene (PTFE). It was found that the phase transitions accompany long tails of heat capacity around the transition temperatures. The shape of the tail was clearly observed. Application of this instrument is expanding to denaturation of

proteins.

4. An instrument for simultaneous measurement of the heat capacity and the volume expansion coefficient.

It is known that the volume and enthalpy changes induced by a temperature jump around the glass transition exhibit delay. This instrument utilizes temperature modulation technique to study the kinetics of the volume and enthalpy responses. Disagreement between the temperatures of characteristic stepwise change in the volume expansion coefficient and the heat capacity was found. A model to explain the disagreement was proposed.

II. Publications and Achievements

(a) Original papers

2007

1) K. Takegawa, K. Fukao, Y. Saruyama, "Aging effects on the thermal expansion coefficient and the heat capacity of glassy polystyrene studied with simultaneous measurement using temperature modulation technique", *Thermochim. Acta*, **461**. 67-71 (2007).
2) K. Takekoshi, K. Ema, H. Yao, Y. Takanishi, H. Takezoe, "Quasi two-dimensional Ising critical behavior of de Vries liquid crystals observed in the heat capacity and dielectric response", *Phys. Rev. E* **75**(3), 031704(2007).

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1) J.-L. Garden, J. Richard, Y. Saruyama, "Entropy production in TMDSC", *J. Therm. Anal. Cal.*, **94**, 585-590 (2008)
2) K. Ema, Y. Sasaki, H. Yao, C.C. Huang, "Study of dielectric dispersion in non-layer-shrinkage liquid crystal compounds", *Ferroelectrics*, **364**, 7-12(2008).

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K. Saito, T. Nakamoto, M. Sorai, H.Yao, K. Ema, K. Takekoshi, S. Kutsumizu, "Thermodynamic symptom of coexistence of two aggregation modes in the Im3m cubic phase formed in thermotropic mesogen, ANBC(n)", *Chem. Phys. Lett.* **469**(1), 157-160 (2009).

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1) Yuji Sasaki, Kenji Ema, Haruhiko Yao, "Static and dynamic critical behaviours in de Vries liquid crystals", *Liquid Crystals*, **37**(5), 571-577 (2010).
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1) Takashi Odagaki, Hideaki Katoh, Yasuo Saruyama, "Linear and Non-linear Dielectric Response of a Model Glass Former", *J. Phys. Soc. Japan*, **80**, 1-4 (2011)
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3) Y. Sasaki, Y. Setoguchi, H. Nagayama, H. Yao, H. Takezoe, K. Ema, "Calorimetric studies on isotropic-B(4) phase transition in the mixture of bent-shaped and rod-like molecules", *Physica E*,

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4) Y. Sasaki, H. Nagayama, F. Araoka, H. Yao, H. Takezoe, K. Ema, "Distinctive Thermal Behavior and Nanoscale Phase Separation in the Heterogeneous Liquid-Crystal B(4) Matrix of Bent-Core Molecules", *Phys. Rev. Lett.*, **107**(23), 237802(2011).

(b) Books

2007

Koji Fukao, Satoshi Fujii, Yasuo Saruyama, Naoki Tsurutani, "Structure Formation and Glass Transition in Oriented Poly(Ethylene Terephthalate)" in "Lecture Notes in Physics 714" pp. 97-116, (ed. by G. Reiter, G. R. Strobl), Springer (2007).

2010

1) Y. Saruyama, in "Handbook of Calorimetry and Thermal Analysis 2nd ed." pp. 150-151, 158-159, 262, (ed. by Japan Society of Calorimetry and Thermal Analysis, A member of the Editorial Board), Maruzen (2010).

2) H. Yao, in "Handbook of Calorimetry and Thermal Analysis 2nd ed." pp. 70-72, 307, (ed. by Japan Society of Calorimetry and Thermal Analysis), Maruzen (2010).

(c) Reviews and Reports

2008

1) Yasuo Saruyama, Koji Fukao, "Glass Transition and Glass Dynamics in Polymers (in Japanese)", Netsu Sokutei, **35**, 26-35 (2008).

2) Kenji Ema, Haruhiko Yao, "Critical behavior of de Vries Smectic A-C phase transition viewed from precise calorimetric and dielectric measurements (in Japanese)", Ekisho, **12**, 195-201 (2008).

2010

Yasuo Saruuyama, "New Technique of Thermal Analysis with Temperature Modulated DSC (in Japanese)", J. Materials Life Society, **22**, 43-47 (2010)

2011

Yasuo Saruyama, "Basic Studies on Temperature Modulated DSC and Temperature Modulation Method and their Application to Slow Dynamics (in Japanese)", Netsu Sokutei, **38**, 86-92 (2011)

(d) Awards

2010

Yasuo Saruyama, JSCTA Award (The Japan Society of Calorimetry and Thermal Analysis), "Basic Studies on Temperature Modulated DSC and Temperature Modulation Method and their Application to Slow Dynamics"

(e) Invited Lectures

2009

Yasuo Saruyama, "Application of the Temperature Modulation Method to Polymers" 11th Japan -

Belgium Symposium on Polymer Science, Tokyo Tech Front, Royal-Blue Hall, Nov. 8 - 11, 2009

2010

Yasuo Saruyama, “Basic Studies on Temperature Modulated DSC and Temperature Modulation Method and their Application to Slow Dynamics (Award Lecture)(in Japanese)”, 46th Japanese Conference on Calorimetry and Thermal Analysis (2010)

(f) Patents

(g) Funds and Financial Supports

2007

Haruhiko Yao, Grant-in-Aid for Scientific Research, Scientific Research(C) 18570148, “Development of an ultra-high-pressure AC nanocalorimeter and its application to the studies on the pressure dependence of heat capacity in protein”.

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Yasuo Saruyama, Grant-in-Aid for Scientific Research, Challenging Exploratory Research 21654059, “Direct Confirmation of Dynamic Heterogeneity with Temperature Modulated X-ray Diffraction”.