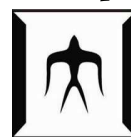


International Student Workshop on Aromatic Functional Polymers 2019



14 November 2019



**Kuramae-Hall
Tokyo Tech**



International Student Workshop on Aromatic Functional Polymers

***Adjunct to the 27th Japan Polyimide and
Aromatic Polymers Conference***

Program and Preprints

14th November 2019

**Tokyo Institute of Technology
Ookayama, Kuramae-Hall, 2F-Conference Room**

Organizing Committee

Workshop Chair

Shinji ANDO (Tokyo Inst. Technol.)

Ryohei ISHIGE (Tokyo Inst. Technol.)

Committee Members

Guey-Sheng LIOU (National Taiwan Univ.)

Jianhua FANG (Shanghai Jiao Tong Univ.)

Chih-Feng HUANG (National Chung Hsing Univ.)

Teruaki HAYAKAWA (Tokyo Inst. Technol.)

Tomoya HIGASHIHARA (Yamagata Univ.)

Registration Fee

Free of charge for all Active Participants

**(Light meal, beverages, and banquet served during the
Workshop are Inclusive)**

Sponsored by

**School of Materials and Chemical Technology,
Tokyo Institute of Technology**

~ Participants ~

Famly name	Given name	Univ.	名前	所属
Huang	Chih-Feng	NCHU	黄 智峯	中興大(台湾)
Liou	Guey-Sheng	NTU	劉 貴生	台湾大
Fang	Jianhua	SJTU	房 建華	上海交大(中国)
ANDO	Shinji	TokyoTech	安藤 慎治	東工大
HAYAKAWA	Teruaki	TokyoTech	早川 晃鏡	東工大
ISHIGE	Ryohei	TokyoTech	石毛 亮平	東工大
JO	Hai-I	NTUST	若海 依	台湾科技大
CHENG	Yu-Hsuan	NTUST	鄭 宇軒	台湾科技大
HUANG	Yi-Shen	NCHU	黄 易紳	中興大(台湾)
CHOU	Li-Chieh	NCHU	周 立杰	中興大(台湾)
WU	Yi-Fang	NCHU	吳 儀芳	中興大(台湾)
HU	Xiang-Cheng	NTU	胡 翔程	台湾大
CHEN	Mu-Huai	NTU	陳 牧懷	台湾大
KE	Chun-Yao	NTU	柯 鈞耀	台湾大
PAI	Min-Hao	NTU	白 旻昊	台湾大
XUE	Tianhao	Tsinghua	薛 天浩	清華大(中国)
YEN	Yongzhu	PNU	閻 永柱	釜山国立大(韓国)
KONG	Delu	SJTU	孔 德祿	上海交大(中国)
FUJIWARA	Eisuke	TokyoTech	藤原 瑛右	東工大(安藤研)
LIANG	Naiqiang	TokyoTech	梁 乃強	東工大(安藤研)
TAKATSUKI	Kahori	TokyoTech	高月 かほり	東工大(安藤研)
NARA	Mayuko	TokyoTech	奈良 麻優子	東工大(安藤研)
FUJITA	Megumi	TokyoTech	藤田 恵実	東工大(安藤研)
HARA	Shohei	TokyoTech	原 昇平	東工大(安藤研)
MUTO	Koichiro	TokyoTech	武藤 江一郎	東工大(安藤研)
TABUCHI	Atsuko	TokyoTech	田淵 敦子	東工大(安藤研)
DOI	Marina	TokyoTech	土井 真里奈	東工大(安藤研)
WATANABE	Ryota	TokyoTech	渡辺 涼太	東工大(安藤研)
FU	Mao-Chun	Yamagata U.	傅 茂鈞	山形大(東原研)
SHOJI	Yamato	Yamagata U.	庄司 倭	山形大(東原研)
SATOH	Uran	Yamagata U.	佐藤 宇覧	山形大(東原研)
CHEN	Hao-Yang	TaipeiTech	陳 昊陽	台北科技大(台湾)
LEE	Chia-Ju	TaipeiTech	李 佳儒	台北科技大(台湾)
DONG	Lei	TokyoTech	董 磊	東工大(早川研)
CHANDRA	Alvin	TokyoTech	A.チャンドラ	東工大(早川研)
AGATA	Yoshihiro	TokyoTech	安形 佳宏	東工大(早川研)
HORI	Kazuhiro	TokyoTech	堀 和滋	東工大(早川研)
NAGASHIMA	Koudai	TokyoTech	永島 功大	東工大(早川研)
MAEDA	Hayato	TokyoTech	前田 颯	東工大(早川研)
CHEN	Wei Hung	TokyoTech	陳 韋宏	東工大(岡本研)
YAO	Yuze	JAIST	姚 禹澤	北陸先端大(長尾研)

~ Student Workshop Program ~

At Tokyo Institute of Technology on 14th November 2019

9:25 Meet-up at Ookayama station (Front gate, for Overseas students)

9:30-9:50 Short campus tour (Main building & Library) & **Registration**

9:55-10:00 Opening Remark by Prof. ANDO Shinji (TokyoTech)

10:00-10:30 Presentation + Q&A : 30 min

Chairperson: ANDO Shinji (TokyoTech)		
10:00 -10:30	L0	<i>"Controlled/Living Polymerizations for the Preparations of Nanomaterials and High Performance Materials"</i> Prof. HUANG Chih-Feng (National Chung Hsing Univ.)

10:30-10:35 Short Break

10:35-11:35 Presentation : 10 min + Q&A: 3 min

Chairperson: YAN Yongzhu (Pusan National University) FU Mao-Chun (Yamagata Univ.)		
10:35 -10:49	L1	<i>"Hypoxia-responsive aggregation-induced emission polymer"</i> XUE Tianhao (Tsinghua Univ.)
10:50 -11:04	L2	<i>"Analysis of Compression Behaviors of a Highly Crystalline Polyimide Prepared from Monomer Salts and Poly(amic acid)"</i> FUJIWARA Eisuke (TokyoTech-Ando lab.)
11:05 -11:19	L3	<i>"Synthesis of triblock copolymer PMMA-b-PDMS-b-PMMA via ATRP and study of microphase-separation in phenolic and amino epoxy resin"</i> HUANG Yi-Shen (National Chung Hsing University)
11:20 -11:34	L4	<i>"Growth of Perpendicular Lamellae in High-χ Block Copolymer Thin Films"</i> CHANDRA Alvin (TokyoTech-Hayakawa lab.)

11:35-11:40 Short Break

11:40-12:40 Presentation : 10 min + Q&A: 3 min

Chairperson: XUE Tianhao (Tsinghua Univ.) CHANDRA Alvin (TokyoTech-Hayakawa)		
11:40 -11:54	L5	<i>"Synthesis and Properties of Redox-Active Diphenylamine-Based α-Cyanostilbene Polymers"</i> HU Xiang-Cheng (National Taiwan Univ.)
11:55 -12:09	L6	<i>"Highly Transparent Fluorescence Polyimide Copolymers with Large Stokes Shifted Photoluminescence Based on Excited State Intramolecular Proton Transfer"</i> LIANG Naiqiang (TokyoTech-Ando lab.)
12:10 -12:24	L7	<i>"Enhanced charge-transporting behavior for solution-processable organic transistor through microwave impetus"</i> JO-HAI I (National Taiwan University of Science & Technology)
12:25 -12:39	L8	<i>"Lyotropic liquid crystal property and organized structure in high proton-conductive semi-alicyclic sulfonated polyimide thin films"</i> YAO Yuze (Japan Advanced Institute of Science and Technology)

12:40-13:55 Lunch with Brief Introductions of Participating Universities**Presentation: 5 min**

1. National Chung Hsing University (Taiwan)
2. Tsinghua University (China)
3. Yamagata University (Japan)
4. National Taiwan University (Taiwan)
5. Pusan National University (Korea)
6. Japan Advanced Institute of Science and Technology (Japan)
7. National Taiwan University of Science & Technology (Taiwan)
8. Shanghai Jiao Tong University (China)
9. Tokyo Institute of Technology (Japan)

13:55-14:55**Presentation : 10 min + Q&A: 3 min**

Chairperson: HUANG Yi-Shen(National Chung Hsing University) FUJIWARA Eisuke(TokyoTech-Ando lab.)		
13:55 -15:09	L9	<i>"Synthesis of New Organo-soluble Polyimides from An Asymmetric and Bulky Diamine Monomer"</i> KONG Delu (Shanghai Jiao Tong University)
14:10 -15:24	L10	<i>"Development of High Refractive Index and Low Birefringence Novel Triazine-based Poly(phenylene sulfide)s"</i> FU Mao-Chun (Yamagata Univ.)
14:25 -15:39	L11	<i>"Synthesis, Characterization of Novel Triarylamine-based Aromatic Poly(ether sulfone)s with AIE-Active Pendent Groups"</i> CHEN Mu-Huai (National Taiwan Univ.)
14:40 -14:54	L12	<i>"Photoconductivity of Polyimide Films Having Enhanced Charge Transfer Interaction"</i> TAKATSUKI Kahori (TokyoTech-Ando lab.)

14:55-15:00**Short Break****15:00-16:00****Presentation : 10 min+Q&A: 3 min**

Chairperson: KE Chun-Yao (National Taiwan University) LIANG Naiqiang (TokyoTech-Ando lab.)		
15:00 -15:14	L13	<i>"Synthesis of Poly(ester-amide) Amphiphilic Polymers Containing Disulfide Bond via Passerini Reaction and Study of Aggregation-Induced Emission in Polar Solvents"</i> CHOU Li-Chieh (National Chung Hsing University)
15:15 -15:29	L14	<i>"Asymmetric hexagonally packed cylinder morphology in a diblock copolymer with liquid crystalline semifluorinated side chains and its domain orientation control in thin films"</i> DONG Lei (TokyoTech-Hayakawa lab.)
15:30 -15:44	L15	<i>"Novel zirconia/mesoporous silica-polyimide nanohybrid films derived from water-soluble poly(amic acid) ammonium salt"</i> YAN Yongzhu (Pusan National University)
15:45 -15:59	L16	<i>"Oxygen-sensitive Luminescence of A Polyimide with Brominated end groups based on Room-temperature Phosphorescence"</i> NARA Mayuko (TokyoTech-Ando lab.)

16:00-16:15

Coffee Break

16:15-17:15

Presentation : 10 min+Q&A: 3 min

Chairperson: HU Xiang-Cheng (National Taiwan Univ.) DONG Lei (TokyoTech-Hayakawa lab.)		
16:15 -16:29	L17	<i>"Conjugated Donor Acceptor Structure of OFET Memories Based on ACQ and AIE Polymer Electrets"</i> KE Chun-Yao (National Taiwan University)
16:30 -16:44	L18	<i>"Effects of Final Curing Temperature on the Thermal Expansion Behaviors of Fluorinated Polyimide Films"</i> FUJITA Megumi (TokyoTech-Ando lab.)
16:45 -16:59	L19	<i>"Stretchable and self-healable semiconducting composite for transistor device"</i> CHENG Yu-Hsuan (National Taiwan University of Science & Technology)
17:00 -17:14	L20	<i>"Skeletal Isomerization of n-tetradecane Using TON-type Zeolite As Catalyst with Addition of Crystal Growth Inhibitor"</i> CHEN Wei Hung (TokyoTech-Okamoto lab.)

17:15-17:20

Short Break

17:20-18:20

Presentation : 10 min+Q&A: 3 min

Chairperson: CHEN Mu-Huai (National Taiwan Univ.) CHEN Wei Hung (TokyoTech-Okamoto lab.)		
17:20- 17:34	L21	<i>"Linear and star block copolymers synthesized via ATRP and study of their self-assembly microstructures"</i> WU Yi-Fang (National Chung Hsing University)
17:35- 17:49	L22	<i>"Orientation Control of Polyimide Film toward Homeotropic Alignment Using Smectic Liquid Crystalline Precursors on Hydrophobic Substrate"</i> HARA Shohei (TokyoTech-Ando lab.)
17:50 -18:04	L23	<i>"A Facile Synthesis of Redox-active Polymers with Intrinsic Microporosity for Enhancing Electrochromic Behaviors"</i> PAI Min-Hao (National Taiwan Univ.)
18:05 -18:19	L24	<i>"Pressure-Induced Variations in Luminescence Properties of Polyimides having Fluorescent End-groups Exhibiting Excited-State Intramolecular Proton Transfer"</i> MUTO Koichiro (TokyoTech-Ando lab.)

18:20-18:25 Closing Remarks

18:30- Reception (Banquet)

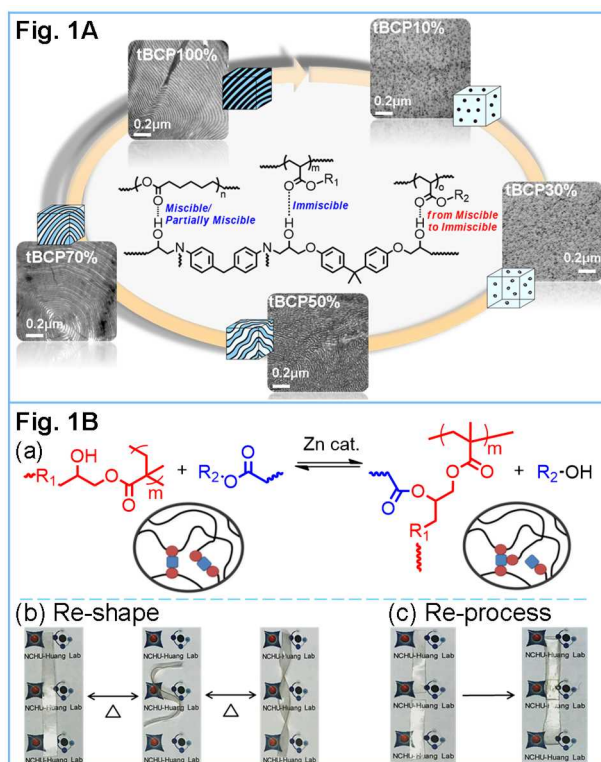
Controlled/Living Polymerizations for the Preparations of Nanomaterials and High Performance Materials

Chih-Feng HUANG^{1,2}

¹ Department of Chemical Engineering, National Chung Hsing University (NCHU), 145 Xingda Road, South District, Taichung 40227, Taiwan; ² Research Center for Sustainable Energy and Nanotechnology, National Chung Hsing University, Taiwan (email: HuangCF@nchu.edu.tw)

In the first part, we synthesized novel triblock copolymer (tBCP) and star block copolymer (sBCP) through ring-opening polymerization (ROP) of ϵ -caprolactone (ϵ -CL) and atom transfer radical polymerizations (ATRPs), of *n*-butyl acrylate (nBA), methyl methacrylate (MMA), and Glycidyl methacrylate (GMA). These polymerizations all achieved controlled/living polymerization fashion that afforded a ABC-type PCL-*b*-PnBA-*b*-PMMA tBCP, 4-arm (PnBA-*b*-PMMA)₄, and 4-arm (PnBA-*b*-PGMA)₄ sBCPs. Then epoxy thermoset (ET)/tBCP and ET/sBCP composites were prepared. As shown in **Fig. 1A**, we observed microstructures of long range order—from lamellar to core/shell cylinder to core/shell spherical morphologies—upon increasing the amount of ET with a range of 30–60 nm via transmission microscopy (TEM) and small-angle X-ray scattering (SAXS).

In the second part, we conducted copolymerizations of MMA and GMA via conventional free radical polymerization and ATRP to afford different types of P(MMA-*co*-GMA) copolymers (*r*: random and *gr*: gradient). As shown in **Fig. 1B(a)**, the P(MMA-*r*-GMA) and P(MMA-*gr*-GMA) copolymers were then reacted with crosslinker and catalyst to form different types of vitrimerized PMMA (PMMA-V) networks that possess dynamic covalent bonds (DCBs). We obtained PMMA-Vs with enhanced mechanical and thermal properties (e.g., $T_g > 140^\circ\text{C}$) as well as the properties of re-shaping (**Fig. 1B(b)**) and re-processing (**Fig. 1B(c)**). Incorporations of soft segments into the PMMA-Vs were further conducted to achieve the increase of PMMA-V toughness.



Controlled/Living Polymerizations for the Preparations of Nanomaterials and High Performance Materials

Chih-Feng HUANG^{1,2} (¹ Department of Chemical Engineering, National Chung Hsing University, 145 Xingda Road, South District, Taichung 40227, Taiwan, ² Research Center for Sustainable Energy and Nanotechnology, National Chung Hsing University, Taiwan) E-mail: HuangCF@nchu.edu.tw

Hypoxia-responsive aggregation-induced emission polymer

Tianhao Xue¹ and Yaning He¹

(¹Department of Chemical Engineering, Tsinghua University)

Conventional fluorophores have been widely used for construction of hypoxia-responsive fluorescent probes. However, due to aggregation induced quenching (ACQ) effect, their further applications might be restricted. In contrast to ACQ effect of conventional fluorophores, aggregation-induced emission (AIE) fluorogens emit strong fluorescence in aggregation state or solid state due to the restriction of intramolecular motions, which is called AIE phenomenon. AIE molecules have been widely used in biosensing and optical devices due to their excellent resistance to photobleaching and linear concentration-dependent increase in brightness features. Compared with hydrophobic AIE small molecules, water-soluble AIE polymers have better solubility and biocompatibility. Tumor hypoxia, as a significant feature of early-stage cancer, has become a target for tumor diagnosis. Therefore, construction of biocompatible hypoxia-responsive AIE polymer is crucial, which may contribute to application of tumor imaging.

We designed a hypoxia-responsive AIE polymer of PEGylated azobenzene caged tetraphenylethene (TPE) via macromolecular azo coupling reaction between PEG diazonium salt and a TPE modified aniline in one pot. Azobenzene moiety can quench the fluorescence of TPE by fluorescence resonance energy transfer (FRET) process efficiently. Besides, azobenzene moiety also act as a switch which can be reduced by azoreductase overexpressed in tumor hypoxic microenvironment. Reduction of -N=N- and aggregation of hydrophobic TPE contribute to the restoration of fluorescence. (Fig. 1) Besides, in vitro experiment was carried out to validate hypoxia responsiveness of the AIE polymer. Moreover, NIR light can also be used as the excited light resource to generate the fluorescence due to the two-photon fluorescence imaging process.

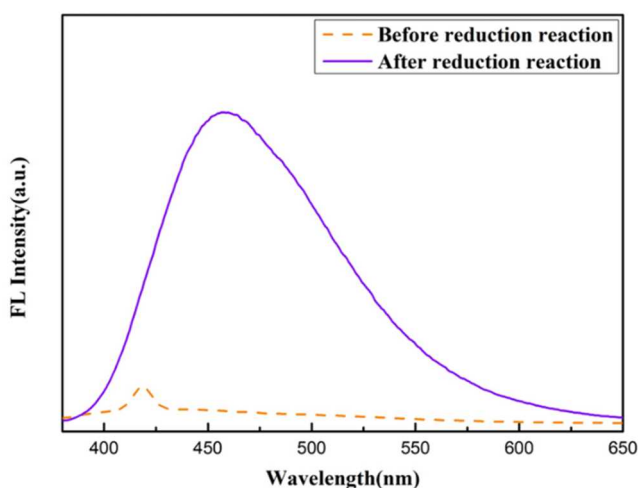


Fig.1 Fluorescence spectra of the AIE polymer before and after -N=N- reduction reaction

Hypoxia-responsive aggregation-induced emission polymer

Tianhao Xue¹, Yaning He¹ (¹ Department of Chemical Engineering, Key Laboratory of Advanced Materials (MOE), Tsinghua University, Beijing 100084, China) E-mail: xueth17@mails.tsinghua.edu.cn

Analysis of Compression Behaviors of a Highly Crystalline Polyimide Prepared from Monomer Salts and Poly(amic acid)

Eisuke FUJIWARA¹, Ryohei ISHIGE¹, D. Alonso Cerron-Infantes², Michael J. Taubländer², Mariam M. Unterlass², and Shinji Ando¹

(¹Dep. Chem. Sci. Eng., Tokyo Institute of Technology, ²Inst. Mater. Chem., Technische Universität Wien)

Introduction: Physical properties of aromatic polyimides (PIs) are closely related to their molecular aggregation structures. We have been investigating the relationship between the optical properties and molecular aggregation structures of PIs at elevated pressures.^[1] In general, crystalline PI particles are synthesized by thermal imidization of poly(amic acid) (PAA) in high b.p. solvents. Recently, PI particles obtained by hydrothermal polymerization of 'monomer salt' (MS), consisting of co-crystals between dianhydride and diamine, were reported as PIs with very high crystallinity.^[2] In this study, compression behaviors of the crystalline and amorphous regions of highly crystalline PI samples prepared from MS and PAA were investigated by wide-angle X-ray diffraction (WAXD) and infrared absorption (IR) spectroscopy under high pressure up to 4 GPa.

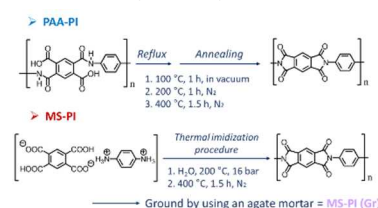
Experimental and methods: Highly crystalline PMDA/PPD powder were prepared by hydrothermal polymerization of MS (MS-PI) or by thermal imidization of PAA in a high b.p. solvent (PAA-PI) (**Scheme 1**). Besides, ground MS-PI (MS-PI (Gr)) was prepared by grinding MS-PI with an agate mortar. To apply pressure to the PI samples, a diamond anvil cell (Syntech Co. Ltd.) was used.

Results and Discussion: The crystallinity (X_c) and density (ρ) at atmospheric pressure for MS-PI ($X_c = 0.90$, $\rho = 1.77$ g/cm³), MS-PI(Gr) ($X_c = 0.46$, $\rho = 1.77$ g/cm³), and PAA-PI ($X_c = 0.40$, $\rho = 1.74$ g/cm³) were estimated based on the WAXD intensity profiles. The volume compression of the crystal lattices of MS-PI, MS-PI (Gr), and PAA-PI at 4.0 GPa were evaluated at 14.0 %, 12.0 % and 9.5 %, respectively (**Fig. 1**). This result demonstrates that MS-PI and MS-PI (Gr) exhibited larger volume compressibility despite their higher densities than PAA-PI. On the other hand, pressure-induced higher-frequency shifts of the IR-band assignable to C=O asym. of the imide ring were analyzed to investigate the compression behaviors of the crystalline and amorphous regions. In general, this shift is attributed to an increase in binding constants (k) caused by shrinkage of covalent bond lengths. The C=O asym. band can be fitted by two Gaussian functions, in which the band at the higher frequency is assignable to C=O groups in the amorphous region. This band exhibits larger shifts than that assigned to the crystalline region in each PI sample (**Fig. 2**). This result indicates that the compressibility of the amorphous region was larger than that of the crystalline region. Consequently, volumetric compression of the crystal lattice in the highly crystalline PIs is dependent on the crystallinity because the compression stress can be preferentially relaxed in the amorphous region.

Reference: [1] E. Fujiwara, S. Ando, *et al.*, *J. Phys. Chem. B*, **122**, 8985 (2018). K. Takizawa, S. Ando, *et al.*, *Macromolecules*, **44**, 49 (2011). *ibid.* **45**, 4764 (2012), *ibid.* **47**, 3951 (2014). [2] B. Baumgartner, *et al.*, *Polym. Chem.*, **5**, 3771 (2014).

Analysis of Compression Behaviors of a Highly Crystalline Polyimide Prepared from Monomer Salts and Poly(amic acid)

Eisuke FUJIWARA¹, Ryohei ISHIGE¹, D. Alonso Cerron-Infantes², Michael J. Taubländer², Mariam M. Unterlass², and Shinji Ando¹ (¹Dep. Chem. Sci. Eng., Tokyo Inst. Tech., Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo 152-8552, Japan. ²Inst. Mater. Chem., Technische Universität Wien, Getreidemarkt 9/BC/2 A-1060, Vienna, Austria.) ¹Tel & Fax: +81-3-5734-2889, E-mail: efujiwara@polymer.titech.ac.jp



Scheme 1 Synthetic scheme of highly crystalline PI samples.

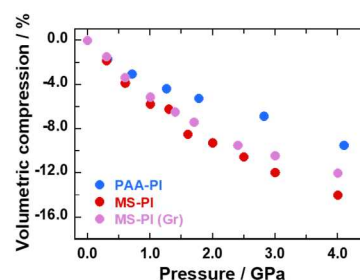


Fig. 1 Volumetric compression of crystalline lattice up to 4 GPa.

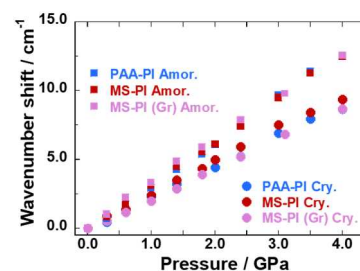


Fig. 2 Peak shifts of C=O asym. mode in crystalline and amorphous regions induced by pressure application.

Synthesis of triblock copolymer PMMA-*b*-PDMS-*b*-PMMA via ATRP and study of microphase-separation in phenolic and amino epoxy resin

Yi-Shen Huang and Chih-Feng Huang*

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Due to potential applications such as mesoporous materials, shape memory materials, catalyst, and separation, the formation of microphase structure has play an important role in nano material technology. For obtaining various micro-

structure, phase-separation mechanism due to intermolecular force has been investigated with various type copolymers and hardener [1]. We have synthesized

triblock copolymer PMMA-*b*-PDMS-*b*-PMMA via ATRP, the well-defined Br-PDMS-Br precursor with relative narrow PDI could be obtained by modification and purification. The characterization has been conducted by ¹H-NMR and GPC. After chain extension of MMA, the result of GPC traces show that the polymerization has been well controlled.

After blending with DGEBA and hardener to form thermoset composites[2], construction of microphase separation has been investigated through Flory-Huggins theory. The rate of crosslinking among DGEBA and hardener and plays an important role in phase-separation [3]. By SAXS analysis, various microphase structure has been observed with various blend ratio. The progress of microphase separation of with phenolic novolac is more apparent than MDA which is more reactive in epoxy curing. As a result, the size of microphase structure that estimated by SAXS is ranged 27-41 nm.

References:

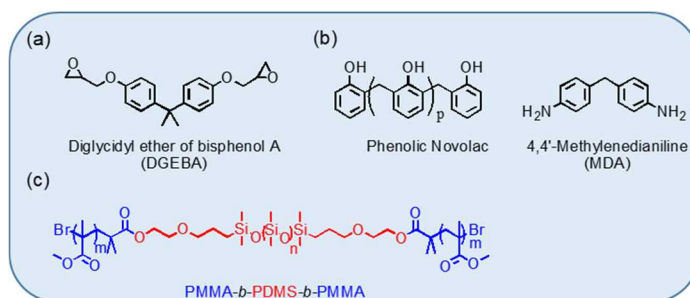
[1]Huang, C.-F.; Chen, W.-H.; Aimi, J.; Huang, Y.-S.; Venkatesan, S.; Chiang, Y.-W.; Huang, S.-H.; Kuo, S.-W.; Chen, T., *Polymer Chemistry* **2018**, 9, 5644.

[2]Rebizant, V.; Abetz, V.; Tournilhac, F.; Court, F.; Leibler, L., *Macromolecules* **2003**, 36, 9889.

[3]Meng, F.; Zheng, S.; Zhang, W.; Li, H.; Liang, Q., *Macromolecules* **2006**, 39, 711.

Synthesis of triblock copolymer PMMA-*b*-PDMS-*b*-PMMA via ATRP and study of microphase-separation in phenolic and amino epoxy resin

Yi-Shen Huang and Chih-Feng Huang* (*Department of Chemical Engineering, National Chung Hsing University, 145 Xingda Road, South District, Taichung 40227, Taiwan) Tel: +886-4-22840510ext408, E-mail: HuangCF@dragon.nchu.edu.tw



Scheme1. The structure of materials (a) epoxy monomer, (b) hardener, and (c) synthesized copolymer

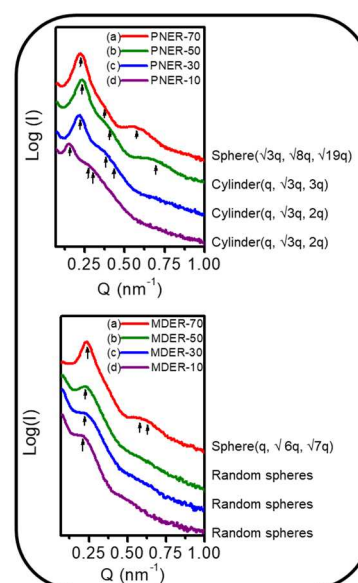


Figure1. SAXS of PMMA-*b*-PDMS-*b*-PMMA blended epoxy composites with curing agent (a)phenolic novolac, (b)MDA

Growth of Perpendicular Lamellae in High- χ Block Copolymer Thin Films

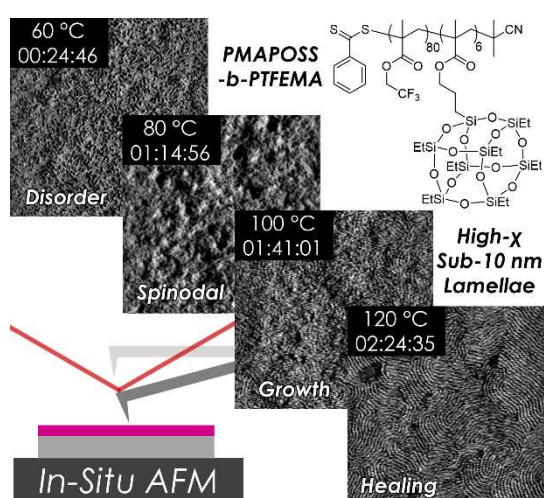
Alvin Chandra, Ryuichi Nakatani, Takumi Uchiyama, Yuta Nabae, and Teruaki Hayakawa

Department of Materials Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1-S8-36 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

ABSTRACT

To support the growth of the computing and microelectronics industry, the development of technologies capable of reliably forming sub-10 nm lithographic patterns are imperative. However, due to the skyrocketing costs and inherent reliance on the wavelength of light used in conventional photolithographic techniques, alternative technologies must also be explored.^[1] To that extent, the self-assembled nanostructures of block copolymers (BCPs) could potentially be utilized as lithographic masks for nanopatterning and microelectronics manufacturing. The use of strongly-segregating, high- χ block copolymers enables access to ordered nanostructures with sub-10 nm feature sizes.^[2] However, there remains a number of challenges that need to be resolved simultaneously prior to industrial high-volume manufacturing; the development of high- χ BCPs capable of forming sub-10 nm features, controlling the microdomain orientation into perpendicular structures on thin films, and reducing the defectivity of the nanostructures.

Our lab has developed a high- χ BCP, poly(methacryl polyhedral oligomeric silsesquioxane) - *block* – poly(2,2,2-trifluoroethyl methacrylate) (PMAPOSS-*b*-PTFEMA) that is capable of forming sub-10 nm feature sizes and orienting perpendicularly on thin films using facile thermal annealing processes.^[3-5] However, as is inherent of a bottom-up process, the as-cast PMAPOSS-*b*-PTFEMA thin films are riddled with structural defects and although annealing processes can be implemented to



reduce the defectivity, the BCP thin film structure will eventually reach an equilibrated state and further defect annihilation becomes highly unlikely. In order to ultimately achieve a nearly defect-free thin film structure, a better understanding of the evolution of ordered structures and defects is required. Therefore, in this study, the growth of ordered structures from an as-cast thin film was directly documented and analyzed using combinatorial high-speed *in-situ* atomic force microscopy (AFM), grazing-incidence small angle X-ray scattering (GI-SAXS), and cross-sectional scanning electron microscopy (CS-SEM).

Figure. Schematic illustration of the *in-situ* AFM

process used to document the growth of perpendicular lamellae in PMAPOSS-*b*-PTFEMA.

References

- [1] D. P. Sanders, *Chem. Rev.* **2010**, *110*, 321.
- [2] C. M. Bates *et al*, *Macromolecules* **2014**, *47*, 2-12.
- [3] R. Nakatani *et al*, *ACS Appl. Mater. Interfaces* **2017**, *9* (37), 31266-31278.
- [4] A. Chandra *et al*, *Adv. Mater. Interfaces* **2019**, *6*, 1801401.
- [5] Nakatani *et al*, *ACS Macro Lett.* **2019**, *8* (9), 1122-1127.

Growth of Perpendicular Lamellae in High- χ Block Copolymer Thin Films

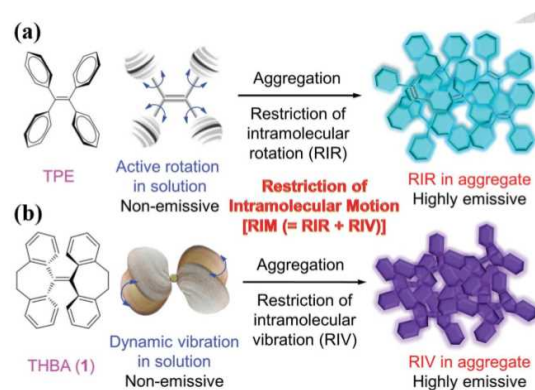
Alvin Chandra, Ryuichi Nakatani, Takumi Uchiyama, Yuta Nabae, and Teruaki Hayakawa (*Department of Materials Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1-S8-36 Ookayama, Meguro-ku, Tokyo 152-8552, Japan*) E-mail: chandra.a.aa@m.titech.ac.jp

Synthesis and Properties of Redox-Active Diphenylamine-Based α -Cyanostilbene Polymers

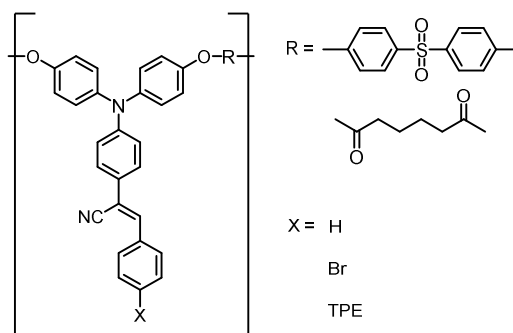
Xiang-Cheng Hu, Guey-Sheng Liou

(Institute of Polymer Science and Engineering, National Taiwan University)

This study is mainly about electrochromism and aggregation-induced emission (AIE). For electrochromism, Electroactive species such as an electron donor or acceptor in the redox sense is involved in electrochromism, which phenomenon ensues from applying a suitable electrode potential between electrodes and chemical materials exhibit reversible optical changes. For aggregation-induced emission (AIE) which intrigue the concerns of scientists, this kind of materials are different from normal materials which exhibit weak emission in aggregated or solid state but perform high luminescence efficiency in dilute solution is termed as aggregation-causing quenching (ACQ). However, it emits tremendously enhanced emission upon aggregation or in the solid state due to restriction of intramolecular rotations (RIR) and restriction of intramolecular vibration (RIV).



Base on the concept mentioned above, we design the structures which contain triphenylamine (TPA) with propeller-like conformation and electron-donating ability. These make it a valuable building block for the construction of AIE luminogens whose colors are capable of being tuned via combining TPA moiety with divergent electron-withdrawing units albeit it shows ACQ. Besides TPA moiety, we also combine π -conjugated cyanostilbene luminogens into the molecular structures which are ubiquitous and effective AIE photoluminescent materials interpreted in many papers.



These diphenylamine-based α -cyanostilbene polymers can be applied to many fields, especially for electrofluorochromism (EFC). Electrofluorochromic materials performing electrochemically controllable fluorescence can simply achieve the research demands. Generally speaking, the intensity of fluorescence could be controlled by the switching between ON and OFF states at suitable applied potentials related to the electrically driven redox reactions.

Design and Synthesis of Diphenylamine-Based α -Cyanostilbene polymers

Xiang-Cheng Hu, Guey-Sheng Liou (Institute of Polymer Science and Engineering, National Taiwan University) E-mail: r07549026@ntu.edu.tw

Highly Transparent Fluorescence Polyimide Copolymers with Large Stokes Shifted Photoluminescence Based on Excited State Intramolecular Proton Transfer

Naigiang Liang, Mayuko Nara, Eisuke Fujiwara, Ryohei Ishige and Shinji Ando

(Department of Chemical Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan)

Introduction:

Polyimide (PI) is a kind of polymer with excellent comprehensive properties. In particular, a group of semi-aromatic PIs can exhibit strong fluorescence due to the suppression of charge transfer.[1,2] For example, our group has reported PI film using 1-hydroxy pyromellitic dianhydride (PHDA, **Fig. 1**), which shows a very large Stokes shifted photoluminescence based on excited-state intramolecular proton transfer (ESIPT) in the PHDA unit. The PHDA-based PI is one of the promising materials for solar spectral converters used in an extreme environment.[3] However, due to the charge-transfer (CT) absorption induced by the strong aggregation of the PHDA unit, this PI film shows yellowish color, as well as low fluorescent efficiency, which may become an obstacle to practical applications. To solve this problem, we have synthesized a series of PI copolymers based on PHDA and 4,4'-oxydiphthalic anhydride (ODPA, **Fig. 2**), as displayed in **Fig. 2**, and investigated the photophysical behavior of these copolymer films.

Results and Discussion:

The fluorescence spectra and photographs of PI copolymer films are presented in **Fig. 3**. The relatively weak fluorescent peak at 405 nm is assignable to the ODPA unit, and the strongest fluorescent peak at 595 nm is assignable to the ESIPT emission from the PHDA unit. All copolymer films exhibit colorlessness and high transparency, which clearly indicates the molecular aggregation is suppressed. Although the molar ratio of PHDA unit in these copolymer films is only several mol%, all copolymer films still retain reddish fluorescence with large Stokes shifts, which proves that efficient energy transfer occurred from the large excess of ODPA unit to the small amount of PHDA unit. Among the series of PI copolymer films, a PI with 3 mol% of PHDA is most suitable for solar converter because of the strong ESIPT fluorescence and comparably weak aggregation. The photoluminescent efficiency of this film reaches to 0.2, which was ca. 3 times higher than the PHDA/DCHM PI homopolymer (0.068). These highly transparent and large Stokes shifted photoluminescent films have great potential for solar spectral conversion.

References:

- [1] J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B*, **46**, 113, 2009.
- [2] J. Wakita, S. Inoue, N. Kawanishi, S. Ando, *Macromolecules*, **8**, 43, 2010.
- [3] K. Kanosue, R. Augulis, D. Peckus, R. Karpicz, T. Tamulevicius, S. Tamulevicius, V. Gulbinas, S. Ando, *Macromolecules*, **5**, 49, 2016.

Highly Transparent Fluorescence Polyimide Copolymer with Large Stokes Shifted Photoluminescence Based on Excited State Intramolecular Proton Transfer

Naigiang Liang, Mayuko Nara, Eisuke Fujiwara, Ryohei Ishige and Shinji Ando (Department of Chemical Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan) E-mail: nliang@polymer.titech.ac.jp

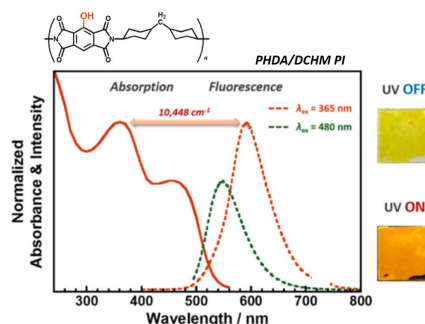


Fig. 1 Photograph and excitation/emission spectra of PHDA/DCHM PI homopolymer

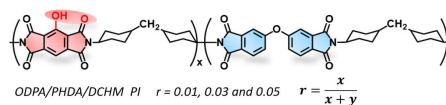


Fig. 2 ODPA/PHDA/DCHM PI copolymers

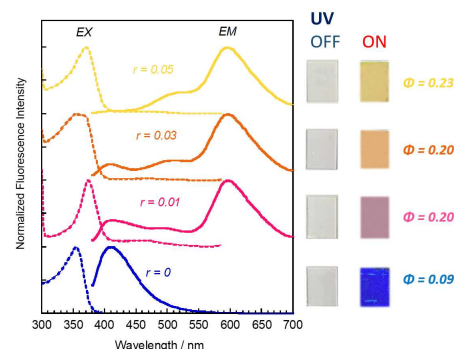


Fig. 3 Fluorescence spectra and photographs of ODPA/PHDA/DCHM PI copolymers.

Enhanced charge-transporting behavior for solution-processable organic transistor through microwave impetus

IJO-HAI¹, Kai Lin Chen¹, Yen Ting Lee¹, Eisuke Fujiwara², Ando Shinji², Yu Cheng Chiu^{1*}

(1 National Taiwan University of Science and Technology 2 Tokyo Institute of Technology)

[Introduction]

The morphology and molecular packing structure of conjugated polymer affect their charge transporting behavior in the intrachain and interchain, which determine the carrier mobility, an index parameter for transistor device. Therefore, the post-processing called thermal annealing is generally required to induce more crystallization in a standard fabrication process for OFET. Thermal annealing is conventionally implemented through thermal conduction methods such as the use of hot plates, however, the energy loss, low efficiency of energy usage and time-consuming question still needs to be modified.

Herein we improve the solubility of semiconducting polymer in the solvent by microwave instead of thermal annealing process. Dissolving materials by microwave inherent a fast and efficient advantages via direct energy transfer. The electromagnetic field is used to rotate the polar molecules so we are based on this property to let the polymer swell well in the polar solvent. As the degree of microwaves absorption depends on the rotation of the dipoles of a material, microwave heating, which can be used to heat material selectively, is a potential approach toward enhancing the efficiency of energy usage.

[Result and Discussion]

The FETs mobility has achieved $0.443 \text{ cm}^2/(\text{V}\cdot\text{s})$ by the microwave method. It's higher than thermal annealing (Fig.1). The microwave method can achieve the same effect within shorter time of annealing preparation. Detailed steady-state UV-vis and PL measurements on solutions of P(NDI2OD-T2)(Fig.2). The measurement immediately after the microwave it will be seen that the blue shift of the CT peak and decreased intensity.

A strategy was developed to improve the charge carrier transport of conjugated polymers. In the future, if microwave combine with printing, the production line of transistors will greatly reduce the cost and simplify.

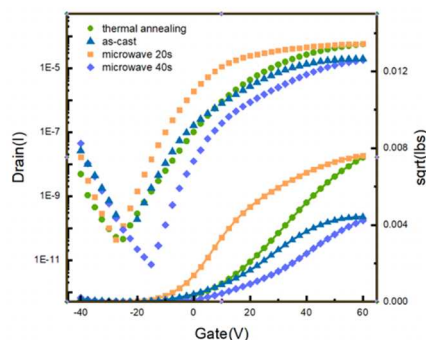


Figure1. Transfer characteristics of NDI2ODT2 TFTs annealed by microwave(green) and by hotplate(orange).

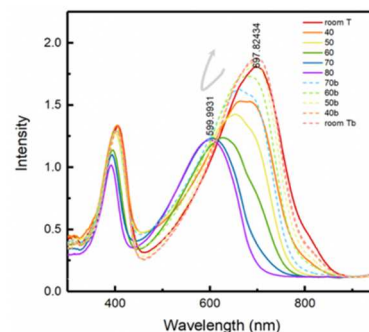


Figure2. Absorption spectra of P(NDI2OD-T2) by various heat-treatment at concentration of 0.05mg/mL.

Enhanced charge-transporting behavior for solution-processable organic transistor through microwave impetus

IJO-HAI¹, Kai Lin Chen¹, Yen Ting Lee¹, Eisuke Fujiwara², Ando Shinji², Yu Cheng Chiu^{1*} (1 National Taiwan University of Science and Technology 2 Tokyo Institute of Technology) E-mail: m10706033@mail.ntust.edu.tw

Lyotropic liquid crystal property and organized structure in high proton-conductive semi-alicyclic sulfonated polyimide thin films

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(¹School of Materials Science, Japan Advanced Institute of Science and Technology, ²Graduate School of Engineering, Nagoya University, ³Venture Business Laboratory, Nagoya University,)

Introduction: Alkyl sulfonated polyimide (ASPI) thin films can show high proton conductivity and molecular ordered structure, but this property is very dependent on molecular weight.^[1] However, recently we synthesized a new semi-alicyclic sulfonated polyimide by using 1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA) and 3,3'-bis(sulfopropoxy)-4,4'-diaminobiphenyl (BSPA) (Scheme 1) showed high proton conductivity and organized structure even with a low molecular.

Results and discussion: The obtained polymer was characterized by ¹H NMR spectrum. The weight average molecular weight was 9300, which was estimated by a gel permeation chromatography (GPC). The thin film exhibited a high conductivity of $2.1 \times 10^{-1} \text{ S cm}^{-1}$ under 25 °C and 95% relative humidity (RH). This value was the highest conductivity compared to the other reported sulfonated polyimides with comparable molecular weight (Fig. 1).^[1-2] Grazing-incidence small-angle X-ray scattering (GISAXS) revealed that anisotropic scattering was observed in the out-of-plane direction as the humidity increased (Fig. 2). The scattering position shifted toward the high d value. This indicates that a lamellar structure was formed in a high RH region by a lyotropic liquid crystalline property. Although a ch-pack interaction reduces by the introduction of the semi-alicyclic CPDA from the aromatic backbone, we could observe the formation of a distinct organized structure. This formation of the organized structure could improve proton conductivity.

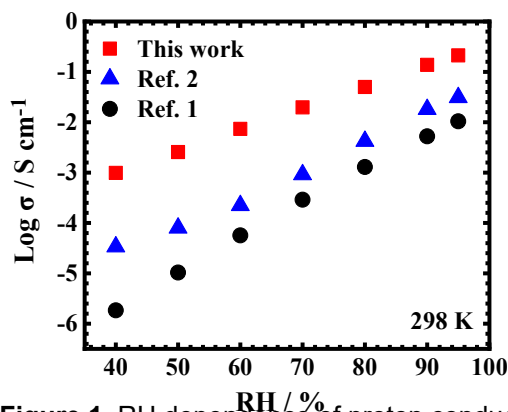


Figure 1. RH dependence of proton conductivity

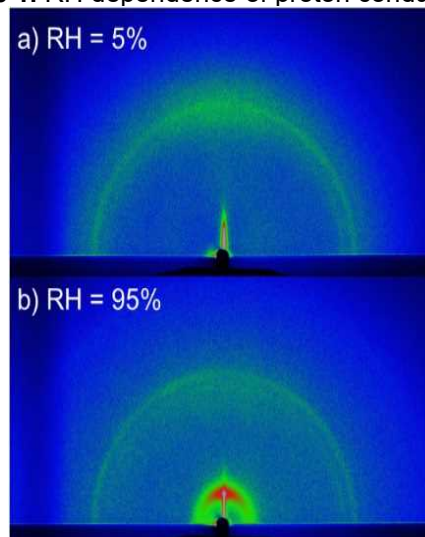
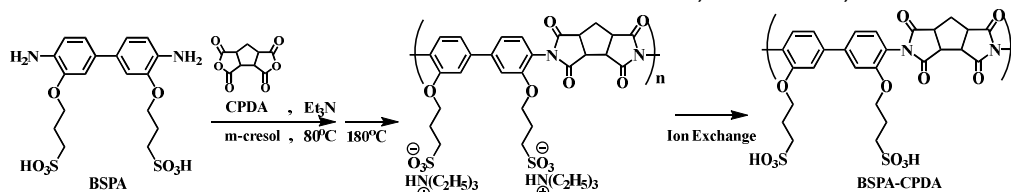


Figure 2. RH controlled in-situ GI-SAXS profiles. a) RH = 5%, b) RH = 95%.



Scheme 1 Synthesis of the new semi-alicyclic sulfonated polyimide

References

- 1) K. Krishnan, H. Iwatsuki, M. Hara, S. Nagano, et al., *J. Phys. Chem. C*, **119**, 21767 (2015).
- 2) K. Takakura, Y. Ono, K. Suetsugu, M. Hara, et al., *Polym. J.*, **51**, 31 (2018).

Lyotropic liquid crystal property and organized structure in high proton-conductive semi-alicyclic sulfonated polyimide thin films

Yuze Yao,¹ Hayato Watanabe,² Mitsuo Hara,² Shusaku Nagano,³ Yuki Nagao¹ (¹School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan. ²Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8601, Japan. ³Venture Business Laboratory, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8601, Japan.) ¹Tel: +81-761-51-1541, Fax: +81-761-51-1149, E-mail: ynagao@jaist.ac.jp

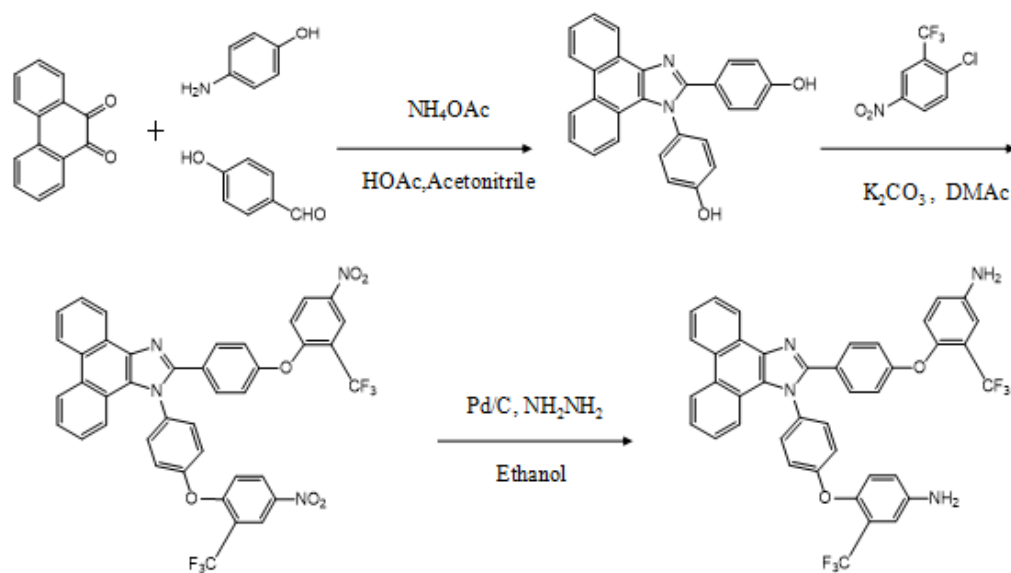
Synthesis of New Organo-soluble Polyimides from An Asymmetric and Bulky Diamine Monomer

Delu Kong¹, Jianhua Fang¹, Chang-sik Ha²

(¹ School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, ²Polymer Science and Chemical Engineering, Pusan National University)

Aromatic polyimides have attracted much attention and show great potential for optoelectronic applications because of their excellent comprehensive performance. However, traditional aromatic PIs usually encounter processing difficulty and appearance of deep color. The reasons for processing difficulty are the high rigidity of the backbone and strong interchain interactions, while the strong intra- and /or inter-molecular charge transfer complex is responsible for the deep color. To overcome these problems, the incorporation of bulky non-coplanar structures and/or flexible segments into the polymer chains and breaking structural symmetry/regularity have been identified to be an effective way to improve solubility and to reduce color of polyimides.

In this presentation, a new asymmetric and bulky diamine containing imidazole heterocyclic ring, trifluoromethyl groups and flexible ether linkages, namely 4,4'-(((1H-phenanthro[9,10-*d*]imidazole-1,2-diyl)bis(4,1-phenylene))bis(oxy))bis(3-(trifluoromethyl)aniline) (PIPOTFA), was synthesized via three-step reactions (Scheme 1). First, 9,10-phenanthrenequinone was reacted with the 4-aminophenol and 4-hydroxybenzaldehyde in acetic acid and acetonitrile in the presence of ammonium acetate to give the intermediate product, 1,2-bis(4-hydroxyphenyl)phenanthro[9,10-*d*]imidazole. Then this intermediate product was further reacted with 4-chloro-3-trifluoromethylnitrobenzene in DMAc in the presence of anhydrous potassium carbonate to yield the dinitro compound. Finally, the dinitro compound was reduced to the diamine monomer with hydrazine in the presence of the catalyst Pd/C.



Scheme 1. Synthesis of a new asymmetric and bulky diamine monomer.

Synthesis of New Organo-soluble Polyimides from An Asymmetric and Bulky Diamine Monomer

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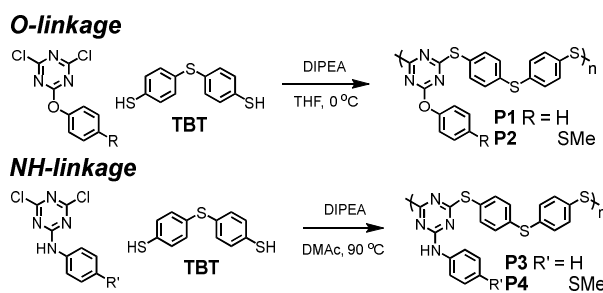
Development of High Refractive Index and Low Birefringence Novel Triazine-based Poly(phenylene sulfide)s

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High-refractive-index (high- n) polymers (HRIPs) with a high optical transparency and low birefringence (low Δn) are highly needed in the applications of advanced optoelectronic devices due to the significant improvement in the device's performance. However, the types of high- n polymers with the balancing of all the desired optical properties are still limited. Previously, Oishi and coworkers reported that the hyperbranched poly(guanamine)s which were prepared from cyanuric chloride and aromatic diamines showed high- n values ($n_D > 1.70$).¹ In our previous work, the linear poly(phenylene sulfide)s (PPSs) were synthesized by triazine derivatives and aromatic dithiols, also exhibiting high- n values ($n_{633\text{nm}}$: 1.64-1.75).² Based on these results, the polymers with triazine unit showed the promising high- n values and high transparency in visible region. To study the structure-property relationship in detail, four different triazine monomers (**T1-T4**) were prepared from cyanuric chloride and aniline or phenol derivatives by the substitution reactions in acetone in good yields (> 90%). The triazine monomers could be divided into two series of *O-linkage* and *NH-linkage*, (**T1**, **T2** and **T3**, **T4**, respectively), and these monomers were further polymerized with aromatic dithiol, 4,4'-thiobisbenzenethiol (TBT) through the solution polycondensation, affording **P1 - P4** (Figure 1). This series of PPSs



Scheme 1. Synthesis of triazine-base PPSs (**P1-P4**)

showed high- n values ($n_{633\text{nm}}$: 1.6902-1.7169), high transmittance in visible region ($T\%_{400\text{nm}} \sim 90\%$) and low birefringence (Δn : 0.0015-0.0042). It is worthy to note that, **P3** and **P4** with *NH-linkages*, exhibited 20°C higher of T_g than **P1** and **P2** with *O-linkages*, which is probably due to the contribution of H-bonding; such an H-bonding effect also led to the higher n values of **P3** and **P4** (1.7112 and 1.7169, respectively) than **P1** and **P2** (1.6902 and 1.7082, respectively). In summary, four new triazine monomers and their corresponding PPSs were successfully synthesized in good yields, exhibiting excellent optical and thermal properties. The results of this work not only show the high potential in the applications to optical materials but also suggest a new design concept for high- n value and low birefringence polymers.

Refs: ¹N. Nishimura et al, *J. Photopolym. Sci. Technol.* **25**, 355, 2012. ²M.-C. Fu et al, *J. Polym. Sci. Part A, Polym. Chem.* **56**, 724, 2018.

Development of High Refractive Index and Low Birefringence Novel Triazine-based Poly(phenylene sulfide)s

Mao-Chun Fu,¹ Mitsuru Ueda,¹ Shinji Ando,² Tomoya Higashihara^{1*} (¹Department of Organic Materials Science, Yamagata University, Yonezawa, Yamagata 992-8510, Japan ²Department of Chemical Science and Engineering, Tokyo Institute of Technology, Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo 152-8552, Japan) E-mail: mc.fu0309@gmail.com

Synthesis, Characterization of Novel Triarylamine-based Aromatic Poly(ether sulfone)s with AIE-Active Pendent Groups

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Recently, our group has reported the fabrication of cross-linking gel-type electrofluorochromic (EFC) devices based on 1-[(4-(bis(4-methoxyphenyl)amino)phenyl)]-1,2,2-triphenylethene (TPE-TPAOME) and 3-[(4-(bis(4-methoxyphenyl)amino)phenyl)]-benzo[b]thiophene-1,1-dioxide (BTO-TPAOME), respectively. TPE-TPAOME and BTO-TPAOME with the methoxy-substituted triphenylamine electron-donating group exhibit outstanding electrochemical stability. According to their aggregation-induced emission (AIE) behavior, gel-type EFC devices with heptyl viologen (HV) were utilized to obtain higher electrochemical performance. However, the PL $I_{\text{off}}/I_{\text{on}}$ contrast ratios were not high enough. To deal with the low contrast ratios, we expect that polymer film-type devices based on TPE-TPA, BTO-TPA structures could reveal enhanced EFC behaviors. Herein, two novel aromatic poly(ether sulfone)s, TPETPA-PES and BTOTPA-PES, based on triarylamine with AIE-active pendent groups were prepared via aromatic nucleophilic substitution polycondensation.

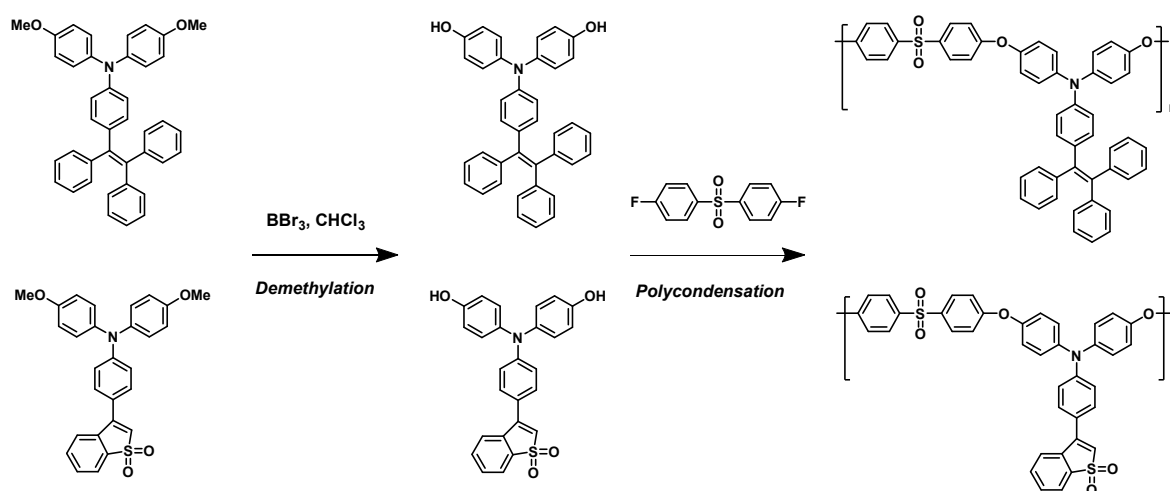


Figure 1. Synthesis route of TPETPA-PES and BTOTPA-PES

Synthesis, Characterization of Novel Triarylamine-based Aromatic Poly(ether sulfone)s with AIE-Active Pendent Groups

Mu-Huai Chen^{a,b}, Guey-Sheng Liou^{a,b*} (^a Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan 10617, ^b Advanced Research Center for Green Materials Science and Technology, National Taiwan University, Taipei, Taiwan 10617.) E-mail: gsliau@ntu.edu.tw

Photoconductivity of Polyimide Films Having Enhanced Charge Transfer Interaction

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Introduction: Recently, polyimides (PIs) containing triphenylamine (TPA) structure or diphenylbenzidine structure have been reported to exhibit high photoconductivity (PC), which is an electric conductivity induced by photo-irradiation [1,2]. These PIs are potentially applicable to multi-valued optical memory and photo sensors. We have previously investigated PC properties of various PIs and reported that charge transfer (CT) interactions between the diamine and dianhydride moieties is essential to enhance their PC [2]. In this study, we synthesized a series of novel PI films using several fluorinated dianhydrides having higher electron-accepting abilities (E_a , Fig. 1) and investigated the relationships between their higher ordered structures and PC properties.

Experimental & methods: The chemical structures of PIs used in this study are shown in Fig. 1. PI films with 0.5 μm thickness were spin-coated onto an indium tin oxide (ITO) substrate, and a silver electrode was deposited on the films as electrodes. The substrates with electrodes were installed in a shield box filled with dry N_2 (Fig. 2). Out-of-plane photocurrent was measured by applying positive voltage onto the ITO electrode under irradiation of visible or UV light monochromated from a xenon light source. Wavelength dependence of absorbance and PC were measured from longer to shorter wavelengths.

Results and discussions: The photoconductive spectra shown in Fig. 3 increased with increasing the CT interactions which is proportional to E_a values in Fig. 1. However, P2FDA-PI exhibited significantly stronger PC than P6FDA-PI, while the E_a value of P2FDA is smaller than that of P6FDA. This is because intermolecular CT interaction (inter-CT) dominates the PC of P2FDA rather than intramolecular CT (intra-CT). The red-shift of absorption edge of P2FDA is one of the evidence of the stronger inter-CT of P2FDA-PI, whereas E_a value is an indicator of intra-CT. Furthermore, 10FEDA-PI exhibited higher PC than that of PMDA-PI in the shorter wavelength region, which is attributable to the higher transparency of 10FEDA-PI. It brings larger penetration depth of UV light and charged carriers are generated more inside the film. Consequently, charge recombination, which blocks the charge transportation, is suppressed to increase the charge mobility through the film. In conclusion, the enhanced inter-CT interactions and higher optical transparency are the essential key factors for the enhancement of photoconductivity of PI films.

Reference: [1] C. Takemasa, T. Chino, R. Ishige, S. Ando, *Polymer*, **2019**, 180, 121713.

[2] K. Takizawa, S. Fukuchi, C. Takemasa, R. Ishige, S. Asai, S. Ando, *Polymer*, **2018**, 157, 122-130.

[3] S. Ando, T. Matsuura, S. Sasaki, *Polym. J.*, **1997**, 29, 69-76.

Photoconductivity of Polyimide Films Having Enhanced Charge Transfer Interaction

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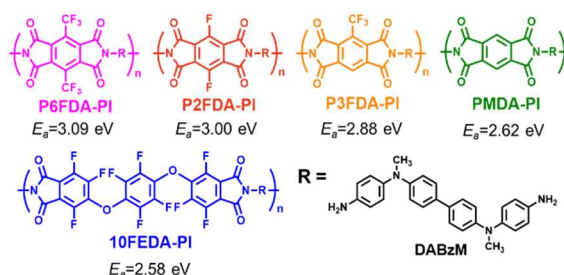


Fig. 1 Chemical structures of the target PIs.

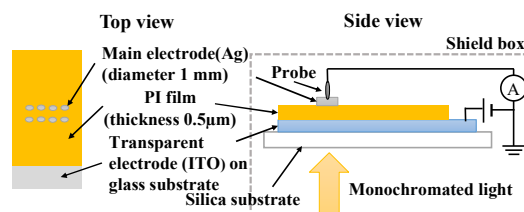


Fig. 2 Setup for photoconductivity measurement.

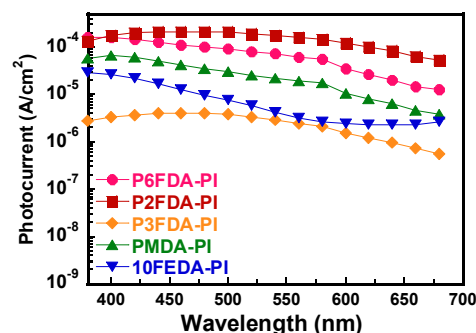


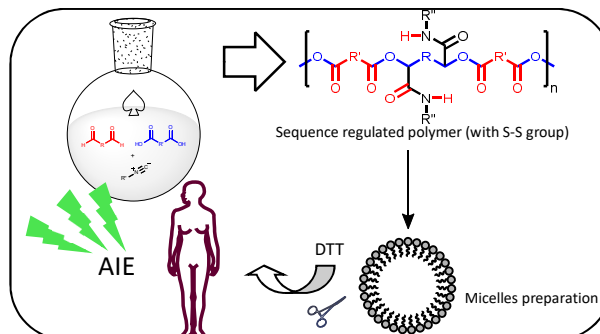
Fig. 3 Photocurrent spectrum of the PI films.

Synthesis of Poly(ester-amide) Amphiphilic Polymers Containing Disulfide Bond via Passerini Reaction and Study of Aggregation-Induced Emission in Polar Solvents

Li-Chieh CHOU, Chih-Feng HUANG*

Department of Chemical Engineering, National Chung Hsing University,

Polymeric nanoparticles play an important role in the nanoscale application such as drug delivery, disease treatment, and bio-imaging. Depending on the morphology, the polymeric nanoparticles can achieve different properties, like micelles in use of cancer cell agent, molecular probes, etc. In this work, we design and synthesizes a series of polymers with different functional groups via the one-step multicomponent polymerization (MCP) based on Passerini reaction.



Scheme1. Reaction mechanism of Passerini 3-CR polymerization and the redox design in micelle application.

MCP is an efficient way to prepare a library of polycondensation polymers. Compared with conventional copolymerization, the copolymerization up to three monomers usually leads to heterogeneity of repeating units (i.e. random copolymer). In this context, sequenced polymers have pushed as a novel research field in polymer science. Passerini reaction is a powerful synthetic tool that can react three different compounds into one molecule in one-step. Moreover, the main chain and side functional group can easily be adjusted via Passerini type MCP.

By employing dialdehydes (A), dicarboxylic acids (B), and isocyanides (C), a variety of ABC-sequenced poly(ester-amide)s can be facilely obtained. Interestingly, they can self-assemble to stable nanoparticles in water ($D_p = \text{ca. } 100 \text{ nm}$), and the morphology will be discussed by the SEM and TEM image. Some polymeric nanoparticles have redox-sensitive property due to the introduction of disulfide bonds. The stability of nanoparticles was to be determined in the presence of dithiothreitol (DTT). Next, the optical performance of aggregation-induced emission (AIE) was demonstrated by the different functional groups to prove the effectiveness and aggregation properties. Importantly, all formed nanoparticles showed a micelle structure with good stability for 5 days monitored by DLS. These results demonstrated the Passerini type MCP to the synthesis of versatile polymeric nanoparticles for biomedical applications.

References:

1. Deng, X.-X.; Li, L.; Li, Z.-L.; Lv, A.; Du, F.-S.; Li, Z.-C. *ACS Macro Lett.* 2012, 1 (11), 1300-1303.
2. Lin, W.; Zhang, W.; Sun, T.; Liu, S.; Zhu, Y.; Xie, Z. *ACS Appl. Mater. Interf.* 2017, 9 (35), 29612-29622.
3. Hu, R.; Leung, N. L. C.; Tang, B. Z. *Chem. Soc. Rev.* 2014, 43 (13), 4494-4562.
4. Meher, N.; Panda, S.; Kumar, S.; Iyer, P. K. *Chem. Sci.* 2018, 9 (16), 3978-3985.

Synthesis of Poly(ester-amide) Amphiphilic Polymers Containing Disulfide Bond via Passerini Reaction and Study of Aggregation-Induced Emission in Polar Solvents

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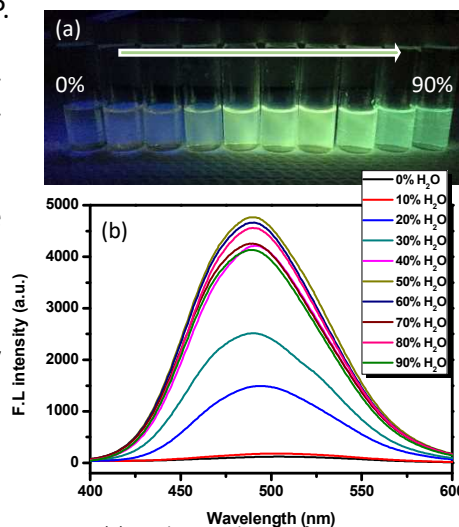


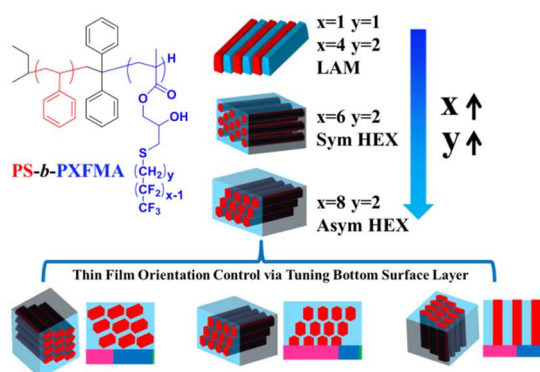
Figure 1. (a) Irradiation photo at $\lambda = 365 \text{ nm}$; (b) FL emission spectra at different water amount ($f_w\%$), the polymer concentration is $1 \text{ mg}/5 \text{ ml}$ at MeOH (the excitation wavelength $\lambda = 330 \text{ nm}$, PMT Voltage = 250 V).

Asymmetric hexagonally packed cylinder morphology in a diblock copolymer with liquid crystalline semifluorinated side chains and its domain orientation control in thin films

Lei Dong¹, Alvin Chandra¹, KevinWylie¹, Yuta Nabae¹ and Teruaki Hayakawa¹

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In this study, a facile approach of domain orientation control in thin film of a block copolymer (BCP) has been demonstrated by employing a BCP with liquid crystalline semifluorinated side chains through tuning the composition of the copolymers of the bottom surface layer (BSL). 1H,1H,2H,2H-Perfluorodecanethiol was attached onto a precursor polymer, polystyrene-*block*-poly(glycidyl methacrylate) (PS-*b*-PGMA), to obtain a novel BCP with a C8F17-containing



liquid crystal (LC) side chain (PS-*b*-P8FMA). Because of the confinement from smectic LC structures with 3.6 nm periodicities, asymmetric hexagonally packed PS cylinder domains with an averaged periodicity of 11.5 nm were characterized by transmission electron microscopy (TEM) and X-ray characterization. Owing to the asymmetric array, two striations of distinctive dimensions (10.9 nm or 12.7 nm) from side view of the array were observed. Poly(2,2,2-trifluoroethyl methacrylate-*random*-methyl methacrylate-*random*-methacrylic acid)s (PTFEMA-*ran*-PMMA-*ran*-PMAA)s were used as BSLs in the study. The surface free energy (SFE) of BSL was tailored by changing the composition of PTFEMA and MMA. Atomic force microscopy (AFM) enabled the investigation of the patterns formed in the thin films. Perpendicularly oriented PS domains in hexagonally packed array were obtained by a non-preferential neutral BSL. Besides, PS-preferential BSL revealed a hybrid striped pattern in response to two types of parallel orientation. The featured dimension of 10.9 nm took a major fraction, as the PS cylinder domain is preferential to BSL. In contrast, PPFMA-preferential BSL revealed a monopoly 12.7 nm striped pattern in another parallel orientation, because this orientation facilitated the wetting of PPFMA blocks onto BSL. Therefore, the orientation control on BCP domains was successfully achieved by tuning on SFE of BSL. Furthermore, various patterns of distinctive dimensions in long-ranged orders could be easily prepared in thin films because of the asymmetry of array. The asymmetric array can be reasonably explained by the scale-confined effects from significant LC side chain ordering on self-assembly nanostructures, as evidenced by the morphology study on BCPs of distinctive fluorinated side chains of CF3, C4F9 and C6F13 with similar M_n and PS volume fractions. As the fluorinated side chain is elongated from C4F9 to C6F13, the side chain LC ordering starts to appear in bulk. Accordingly, a morphology transition from lamellae to regular symmetric HEX, and further to asymmetric HEX array was observed with elongated fluorinated side chain. The comparative thin film study also reveals the essential role of LC ordering for BCP domain orientation.

Asymmetric hexagonally packed cylinder morphology in a diblock copolymer with liquid crystalline semifluorinated side chains and its domain orientation control in thin films

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Novel zirconia/mesoporous silica-polyimide nanohybrid films derived from water-soluble poly(amic acid) ammonium salt

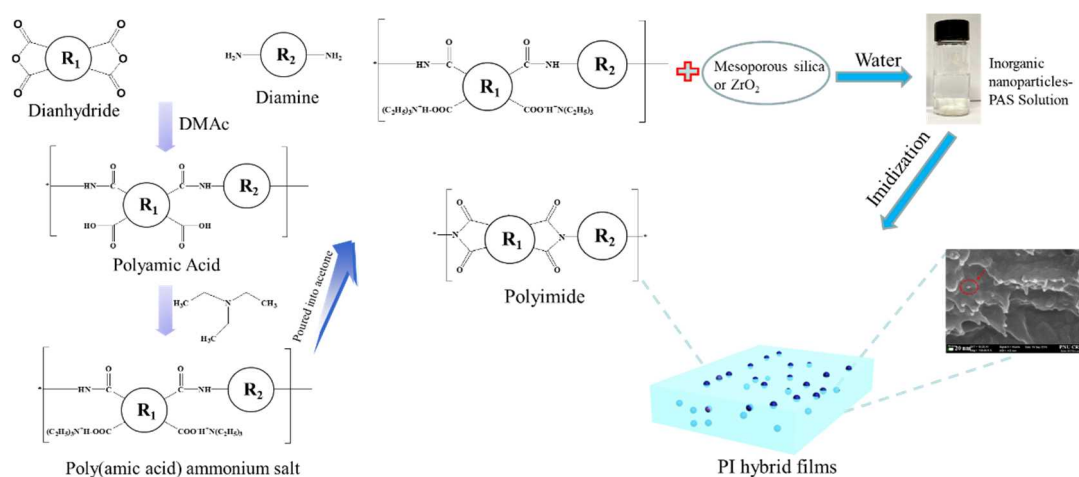
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Insufficient dielectric property is major impediment for the commercialization of polyimide (PI) in the future flexible organic electronic devices. High dielectric constant (high k) polymers have important application in advanced electronic devices such as wearable electronics, artificial muscles and energy storage because of their excellent flexibility and ease of processing. On the other hand, in order to reduce the resistance-capacitance (RC) delay, low dielectric constant (low k) insulating materials are necessarily required for ultralarge scale integration (ULSI) circuits, multilevel interconnection technology. The integration of inorganic nanoparticles to polyimide matrices is a powerful tool to confer their complementary and fascinating properties.

More importantly, the dielectric properties of PI can be tuned by controlling the addition of the different inorganic nanoparticles. It is well known that ZrO_2 has been regarded as one of the most promising high- k materials because of its wide band gap (5.8 eV), good thermal stability, and high dielectric constant (~ 25). On the other hand, mesoporous silica films are of interest to the hybrid composites as low dielectric constant materials due to the special voids and fine-adjustable porosity. In this work, zirconia/mesoporous silica-polyimide nanohybrid films with well uniformity and dispersion were firstly developed by incorporation of ZrO_2 or mesoporous silica. The method of fabricated PI hybrid films is based on water-soluble poly(amic acid) ammonium salt, aqueous ZrO_2 nanodispersion and aqueous mesoporous silica, which leads to well compatibility and good phase mixing behavior. In addition, for optical electronic devices applications, materials need to be concurrently optically, electrically, mechanically, chemically and thermally stable. Therefore, the transparent polyimide films with tunable dielectric constants is in progress. The effects of the addition of inorganic nanoparticles on the optical, dielectric, mechanical properties and coefficient of thermal expansion of the transparent polyimide will be investigated in detail.



Scheme 2. Illustration of the synthesis of the polyimide hybrid films.

Novel zirconia/mesoporous silica-polyimide nanohybrid films derived from water-soluble poly(amic acid) ammonium salt

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Oxygen-sensitive Luminescence of A Polyimide with Brominated end groups based on Room-temperature Phosphorescence

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[Introduction]

Polyimide (PI) has been attracting much interest owing to its potential applications as novel luminescent materials bearing high thermal and radiation stabilities. Previously, we have designed highly fluorescent (FL) [1] and room-temperature phosphorescent (RTP) PIs [2,3]. In particular, RTP PIs are potentially applicable to oxygen sensors because they exhibit highly oxygen-sensitive luminescence. However, most of RTP PI films exhibit low optical transparency and low luminescence quantum yield due to strong absorption in the visible region which mainly originates from their aggregation [2]. In this study, we designed and synthesized a novel end-capped PI which consists of a highly FL PI with end groups containing bromine atom as heavy halogen and tried to develop colorless and transparent RTP PI films.

[Experiment]

End-capped PI films (OD-4Br) were prepared by the conventional two-step procedure using ODPA (4,4'-oxydiphthalic dianhydride) as a dianhydride, DCHM (4,4'-diaminocyclohexylmethane) as a diamine, and 4BrNA (4-bromonaphthalic anhydride) as end groups as presented in Fig. 1 insets.

[Results and Discussion]

The absorption and emission spectra of OD-PI and OD-4Br are shown in Fig. 1. These films show absorption bands only in the UV regions, which supports the colorlessness and high transparency. In the emission spectra, OD-PI exhibited blue fluorescence (λ_{em} = 404 nm) by excitation at 340 nm. OD-4Br exhibited dual emission (λ_{em} = 404, 508 nm) by excitation at 350 nm, which are assignable to luminescence from the main chain and the end groups, respectively. In addition, OD-4Br exhibits significantly higher quantum yield (Φ = 21 %) than OD-PI (Φ = 11 %). These results suggest that efficient energy transfer occurred from the main chain to the end group. As shown in Fig. 2, luminescent peaks at 560 and 600 nm were dramatically enhanced under vacuum, which revealed the RTP property of the end groups. When the OD-4Br luminescent colors were displayed in the CIE coordinates, OD-4Br showed different colors (blue and yellow) under atmospheric and vacuum, respectively. This is because the quenching of RTP by oxygen is reduced under vacuum. In summary, these results demonstrated that a FL PI having brominated end groups exhibited colorlessness, high transparency, and high quantum yield, as well as high RTP properties, which is promising for oxygen sensor applications.

[References]

- [1] J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B*, **19**, 15212-15224 (2009). [2] K. Kanosue, S. Ando, *ACS. Macro. Lett*, **5**, 1301-1305, (2016). [3] K. Kanosue, S. Hirata, M. Vacha, R. Augulis, V. Gulbinas, R. Ishige, S. Ando, *Mater. Chem. Front.*, **3**, 39-49 (2019).

Oxygen-sensitive Luminescence of A Polyimide with Brominated end groups based on Room-temperature Phosphorescence.

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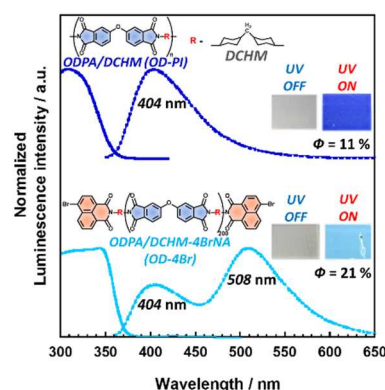


Fig. 1. Absorption / emission spectra of OD-PI and OD-4Br.

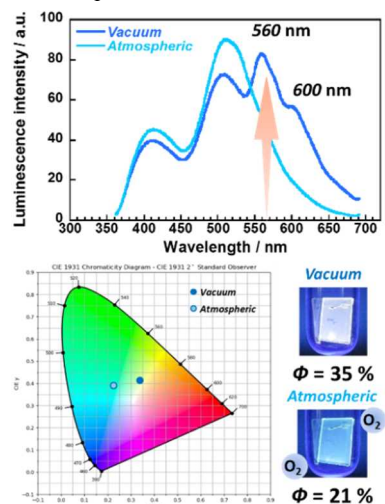


Fig. 2. Luminescence spectra and CIE coordinates of OD-4Br under atmospheric and vacuum condition.

Conjugated Donor Acceptor Structure of OFET Memories Based on ACQ and AIE Polymer Electrets

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Two kinds of poly(triphenylamine)s (PTPA-3CN, PTPA-CNBr) with pendent acceptors (tricyanovinyl, α -cyanostilbene) have been readily synthesized by oxidative coupling polymerization using FeCl_3 as oxidant. Through our previous report, we know that using the AIE group can enhance the memory window utilizing its own light emission. Moreover, using the coplanar structure not only to make the charge in the trapped state more stabilize, but also facilitate the exciton to more easily dissociate. In this study, two triphenylamine-based conjugated polymers, PTPA-3CN and PTPA-CNBr, with different aggregation behavior are provided to design materials for photo-responsive OFET memories (**Figure 1**). As charge storage elements, triphenylamine groups should be beneficial to the hole-trapping, while strongly acceptor units provide the electron trapping sites and act as a decisive factor of illuminate. PTPA-3CN could exhibit ACQ (aggregation-caused quenching) behavior because of triphenylamine and tricyanovinyl as the donor group and the acceptor, respectively. As for PTPA-CNBr, α -cyanostilbene introduced into the molecular structure as acceptor resulted in AIE (aggregation-induced emission) effect. Furthermore, we also confirm more effective exciton existence in electret layer by absorption and photoluminescence spectra in film states.

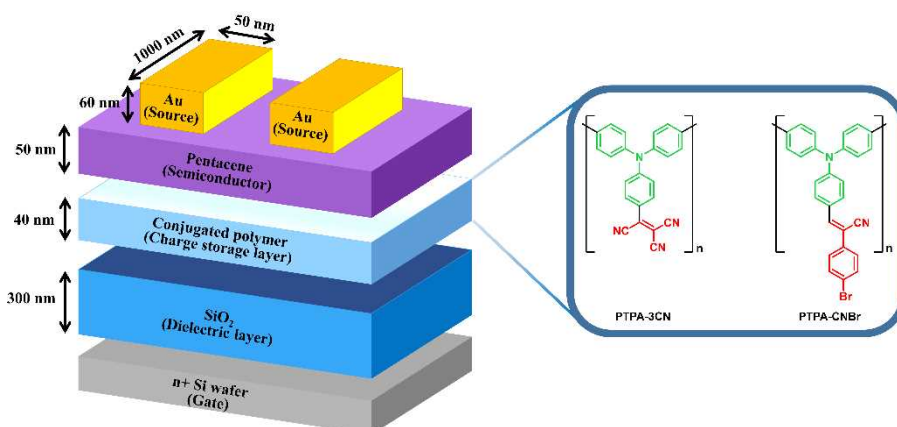


Figure 1. Configuration of conjugated polymer based OFET memory devices.

Conjugated Donor Acceptor Structure of OFET Memories Based on ACQ and AIE Polymer Electrets

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Effects of Final Curing Temperature on the Thermal Expansion Behaviors of Fluorinated Polyimide Films

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Introduction: In recent years, polymer materials have been applied as transparent substrate film exhibiting high thermal stability. One of the challenges for polymer films is suppression of the coefficient of thermal expansion (CTE), which causes peeling or cracking in the device. The CTE of PI films is affected by the preparation procedure. Moreover, although aromatic polyimide (PI) has excellent properties for the substrate, it exhibits a deep yellow color. In this study, we investigated the relationship between thermal expansion behaviors and the free volume size of colorless fluorinated PI films prepared at different imidization temperatures (T_{imd}).

Experimental and methods: Fluorinated PI films, 6FDA/PPD and 6FDA/MPD (Fig. 1), were formed on a silicon wafer by spin-coating of poly (amic acid) solutions, followed by thermal curing at different T_{imd} (250 – 350 °C). The polyimide films ($12 \pm 2 \mu\text{m}$ thick) peeled off from the substrate were annealed at T_{imd} to release residual stress. The out-of-plane and the in-plane thermal expansion coefficient (CTE_{\perp} and CTE_{\parallel}) were measured in a temperature range from 40 to 230 °C by optical interferometry method [1] and thermomechanical analysis (TMA), respectively. The coefficient of volumetric expansion (CVE) was calculated as $\text{CVE} = 2 \text{CTE}_{\parallel} + \text{CTE}_{\perp}$. The free volume size and the number density for PI films near "air surface (s)" and "the substrate interface (i)" interfaces were measured by positron annihilation lifetime spectroscopy (PALS) method at room temperature within the range of 1 μm .

Results and discussions: CTE_{\parallel} and CTE_{\perp} increased with increasing T_{imd} , and the CVE increased by 15%. The distributions of free volume size near the surfaces were broadened either 's' and 'i' with T_{imd} (Fig. 2). In other words, films near the interfaces became sparser with increasing T_{imd} . On the other hand, the bulk density estimated from refractive indices increased with increasing T_{imd} . It can be considered that the density near the interface decreases with increasing T_{imd} , whereas the local mobility near PI chain ends is enhanced at higher temperatures, while the density at the bulk state becomes higher because of the increase of ordered structures in bulk. This result indicates that the high T_{imd} films imidized above T_g become equilibrium, while the low T_{imd} films imidized below T_g were stabilized in a non-equilibrium state like pre-physical aging [2], thereby the density inside the sample increased, and free volume expansion is enhanced, leading to an enlargement in CTE_{\perp} and CTE_{\parallel} as presented in Fig. 3.

Reference: [1] S. Ando, K. Sekiguchi, M. Mizoroki, T. Okada, R. Ishige, *Macromol. Chem. Phys.* 170035 (1-10) (2017). [2] Odegard, G. M, *J. Polym. Sci. Part B Polym. Phys*, **49**, 1695 (2011).

Effects of Final Curing Temperature on the Thermal Expansion Behaviors of Fluorinated Polyimide Films.

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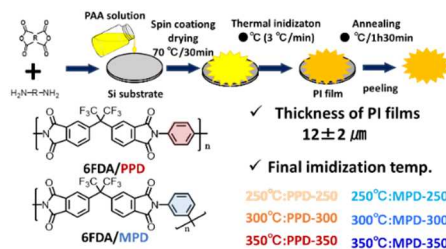


Fig. 1 Preparation and chemical structures of PIs.

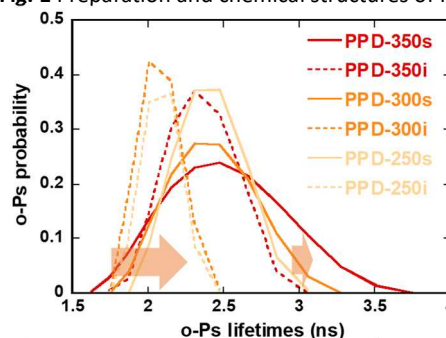


Fig. 2 Variations of o-Ps lifetime distribution.

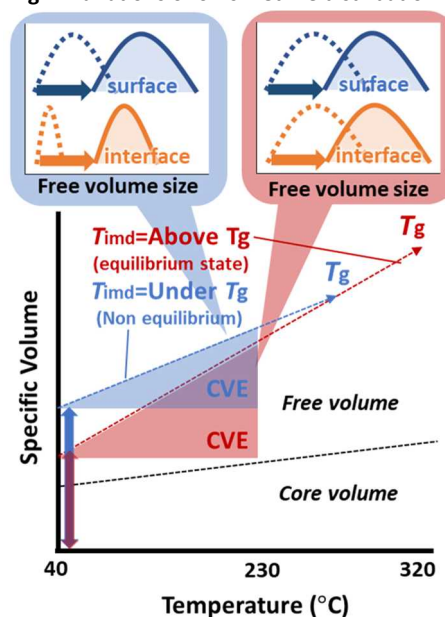


Fig. 3 Schematic images of volumetric thermal expansion behaviors.

Stretchable and self-healable semiconducting composite for transistor device

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Abstract: Nowadays the demands for soft and wearable electronic are increasing, however, the mechanical failure of fully conjugated semiconducting materials upon strain due to their rigid properties leading crack propagation. To solve this problem, we prepare the conjugated polymer and natural rubber by using blending method to form composite film with stretchability. As the results, our fabricated semiconducting composite thin film can be stretched up to 150% strain without cracks and maintain the mobility on the same order of magnitude for the electrical performance (**Figure 1**). Besides, the transport direction of charge carrier has no impact on charge mobility and it shows strain-independent behavior. Furthermore, the composite film demonstrated long-term device stability under ambient environment over 150 days. One of the interesting result in this research is the composite film exhibits self-healing property at the room temperature due to the presence of natural rubber. The electrical properties of the composite upon tensile strain are reported in this study.

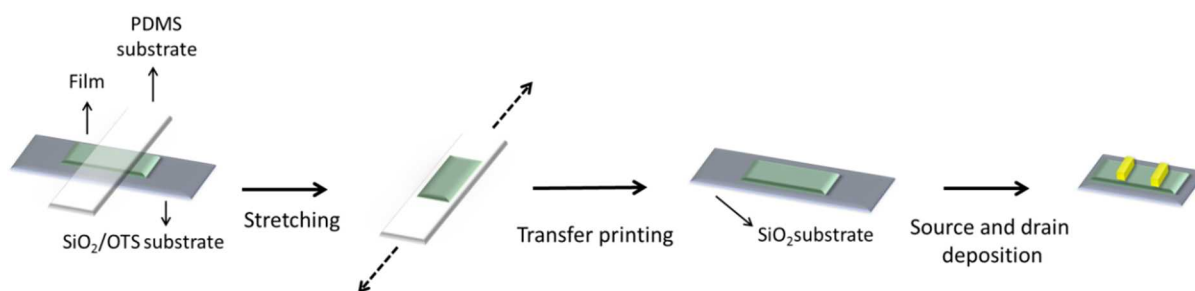


Figure 1. Fabrication process for OTFTs with stretched polymer thin films.

Stretchable and self-healable semiconducting composite for transistor device

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Skeletal Isomerization of *n*-tetradecane Using TON-type Zeolite As Catalyst with Addition of Crystal Growth Inhibitor

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[Introduction]

Zeolite is a kind of material having regular pore size and solid acidity, and can be functionalized via shape control. For zeolites having one-dimensional pores, as the aspect ratio (long axis/short axis) decreases, the number of pores per weight increases. Therefore, shape control of aspect ratio reduction is an effective way to obtain products selectively produced by reaction happening on the pore entrances.

TON-type zeolite with one-dimensional pores show high selectivity in skeletal isomerization of straight-chain alkanes because isomerization tends to occur on acid sites near the pore entrance of the zeolite crystal. Additionally, mono-branched alkanes produced by isomerization are less likely to enter the pores of the zeolite, and thus further isomerization and cracking, cleaving hydrocarbon chains, can be suppressed. Consequently, mono-branched alkane as the product of skeletal isomerization is supposed to be selectively obtained. Therefore, by using a TON-type zeolite with a smaller aspect ratio as a catalyst to increase acid sites near the pore entrance of the crystal, the catalyst is expected to exhibit higher catalytic activity and selectivity in the skeletal isomerization of linear alkanes.

In this research, polyethylene glycol (PEG) was used as an inhibitor to synthesize TON-type zeolite with a smaller aspect ratio. Moreover, the catalyst is evaluated by the isomerization of *n*-tetradecane.

[Experiments]

KOH, $\text{AlF}_3 \cdot \text{H}_2\text{O}$ and 1,8-diaminooctane (DO) were dissolved in water. A dispersion of colloidal silica in water was added to the mixture, stirred for 1.5 h, and settled for 24 h. The synthesis gel ratio was $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{DO}/\text{KOH}/\text{H}_2\text{O} = 1:0.01:0.3:0.3:38$. The synthesis gel was heated at 160 °C for 72 h while being stirred at 20 rpm. The crystals were calcined in a dry airstream at 600 °C for 10 h. 1% (w/w) of platinum was then impregnated on TON-type zeolite using tetraammineplatinum(IV) chloride as a platinum source, and the catalysts were calcined at 400 °C for 2 h in dry air. Finally, hydroisomerization of *n*-tetradecane was performed with TON-type zeolites prepared to evaluate the catalytic activity.

[Results and discussion]

For the result of synthesis, TON-type zeolite synthesized without inhibitor has needle-like shape with a length of about 300 nm with an aspect ratio at 5.8. In comparison, crystal synthesized with PEG has shorter needle-like particles with an aspect ratio at 3.1. Table 1 shows the results of *n*-tetradecane isomerization. The selectivity was improved when zeolite prepared by adding PEG as an inhibitor. This is presumed the acid sites near the pore entrance increased as the aspect ratio decreased. As a result, it was possible to improve the isomerization yield by using TON-type zeolite with a smaller aspect ratio.

Table 1. Skeletal isomerization of *n*-tetradecane

Catalyst	<i>n</i> -C14 Conversion (%)	Isomers Selectivity (%)	Isomers Yields (%)
Without Inhibitor	80.7	50.3	40.6
With PEG	81.0	56.4	45.7

Catalyst 0.4 g, $W/F = 13.5 \text{ g} \cdot \text{h}/\text{mol}$, 623 K, *n*-C₁₄ 0.48 mmol/min, H₂ 1.05 mmol/min, 3 MPa-g

Skeletal Isomerization of *n*-tetradecane Using TON-type Zeolite As Catalyst with Addition of Crystal Growth Inhibitor

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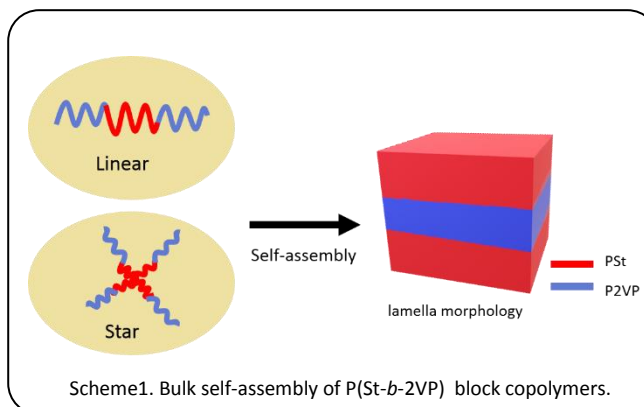
Linear and star block copolymers synthesized via ATRP and study of their self-assembly microstructures

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We prepared well-defined and high molecular weight ($M_n = 30k \sim 80k$) amphiphilic 2, 4-arm polystyrene-*block*-poly(2-vinylpyridine) (P(St-*b*-2VP)) and narrow polydispersity ($M_w/M_n < 1.5$) by (supplemental activators and reducing agents) atom transfer radical polymerization ((SARA) ATRP), through the different ratios of P(St-*b*-2VP) block copolymers bulk self-assembled.



The morphology of the different architecturally block copolymers in the bulk self-assembly had discussed. Through the unique properties of the star-shaped copolymers structure, high molecular chain density, and low solution viscosity, it is expected that the multiple arms can provide greater enhance microphase separation, which is an interesting microstructure in self-assembly. The structures of these linear/star block copolymers and their precursors would be characterized by NMR, FT-IR, and GPC analysis. The morphology of these block copolymers would be characterized by transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS) to observe the microstructures and applications. In bulk self-assembly, it successfully corresponded to SAXS and TEM to obtain lamellae self-assembled microstructures.

References:

1. Polymeropoulos, G.; Moschovas, D.; Kati, A.; Karanastasis, A.; Pelekanou, S.; Christakopoulos, P.; Sakellariou, G.; Avgeropoulos, A. J. Polym. Sci., Part A: Polym. Chem. 2015, 53, 23-32.
2. Huang, C.-F.; Chen, W.-H.; Aimi, J.; Huang, Y.-S.; Venkatesan, S.; Chiang, Y.-W.; Huang, S.-H.; Kuo, S.-W.; Chen, T. Polym. Chem. 2018, 9, 5644-5654.

Linear and star block copolymers synthesized via ATRP and study of their self-assembly microstructures

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Orientation Control of Polyimide Film toward Homeotropic Alignment Using Smectic Liquid Crystalline Precursors on Hydrophobic Substrate

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[Introduction] Highly oriented polyimides (PIs) can afford a variety of applications. Although, rigid polymers strongly tend to align parallel to a substrate due to multiple attractive interactions, vertically aligned PI films have much interests as high thermal conductive layers in the thickness direction. In this study, we focused on one of the precursors of PIs, poly(amic ester)s (PAEs), which are semi-rigid and exhibit smectic liquid crystal in the concentrated NMP solution [1,2]. The smectic layer structure can form homeotropic alignment (HA) structure by growing in layer by layer mechanism (epitaxial growth) from the air interface. Therefore, the PAE solutions are potential precursors for HA-PI films. To enhance the epitaxial growth, we introduced hydrophobic perfluoro-alkyl (R_f) end groups, and also used hydrophobic Si substrates modified with R_f group to reduce the attractive interactions at the interface.

[Experimental] A PAE having R_f ($= \text{CF}_3(\text{CF}_2)_{7-}$) end group (Fig. 1) was prepared from a PAE and perfluorooctyl acid chloride in NMP solution. PAE films were prepared by the push coating method [3] at 50 °C for 1 h, followed by heating at 350 °C for 1 h to convert PI films. Uniaxial orientation order parameter S , defined by $S = (3\langle \cos^2\vartheta \rangle - 1)/2$, where ϑ is the angle between the molecular long axis and averaged orientation direction, was evaluated by infrared pMAIRS method. The S values of -0.5 , 0 , and 1 represent perfectly homogeneous, random, and homeotropic orientation, respectively. Molecular orientation distribution was estimated by GI-WAXD at Photon Factory (Tsukuba, Ibaraki, BL6A, $\lambda = 1.5 \text{ \AA}$, Proposal number 17G693).

[Results and discussion] Fig. 2 shows the thickness dependence of S values of PAE films. The S values were calculated from dichroic ratio of absorbance peak at 1490 cm^{-1} which was assigned to aromatic C=C stretching vibration with a transition moment parallel to the main chain. The S values of PAE film on hydrophobic substrate are higher than that on hydrophilic substrate, and exhibit HA like behavior in the thinner region. These results indicate that the epitaxial growing was enhanced by increasing the specific surface area. Fig. 3 shows the 2D GI-WAXD pattern of a PAE film coated on hydrophobic substrate. Shape layer reflection ($d = 2.0 \text{ nm}$) was observed on the meridian and broad one was on the equator, indicating a double orientation. The former one shows the epitaxial growth of the smectic layer and the fraction of homeotropically aligned region was evaluated at 0.35, which is consistent with the results of pMAIRS. We demonstrated that push-coated PAE films formed on hydrophobic substrate are promising candidates for functional HA films.

[References] [1] C. Neuber et al, *Macromol. Chem. Phys.*, **203**, 598-604 (2002). [2] K. Tanaka, S. Ando, R. Ishige, *Macromolecules*, **52**, 5054-5056 (2019). [3] M. Ikawa, T. Hasegawa et al, *Nat. Comm.*, **10**, 1038 (2012).

Orientation Control of Polyimide Film toward Homeotropic Alignment Using Smectic Liquid Crystalline Precursors on Hydrophobic Substrate

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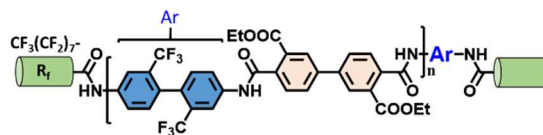


Fig. 1 Chemical structures of PAE

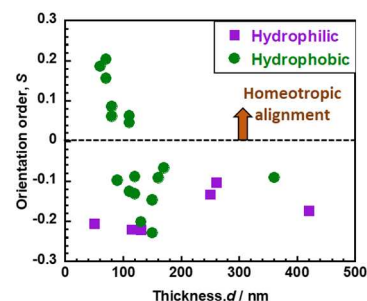


Fig. 2 Thickness dependence of S values of PAE films

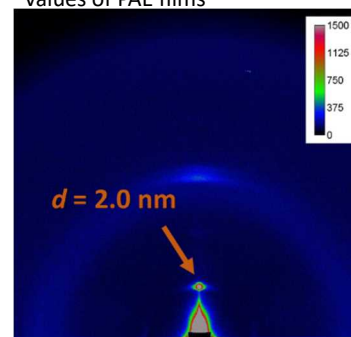


Fig. 3 2D GI-WAXD pattern of push-coated PAE film measured

A Facile Synthesis of Redox-active Polymers with Intrinsic Microporosity for Enhancing Electrochromic Behaviors

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ABSTRACT

Electrochromic (EC) materials reveal reversible color-changes in the optical absorption spectra during electrochemical oxidation-redox procedures, and because many advantages of the EC materials, such as high coloration efficiency, low power consumption and long cycle life, they are regarded as potential and promising choice for optical applications. Since 2002, our research group has been working on the development of high performance EC polymers, such as polyamides and polyimides. According to our recent research efforts, EC materials with high transparency and colorless at neutral state could be obtained when triphenylamine derivatives were utilized as electroactive moieties within these EC polymers, and could change to various colors by tuning their chemical structures, which are considered as the anodically electrochromic materials. However, some vital and crucial issues still have to be dealt with for enhancing EC performance, such as coloration efficiency, electrochemical stability, response time, and on/off optical contrast ratio.

In order to improve the problems mentioned above, two facile strategies, porous structure and polymer hybrid, have been utilized in our group to prepare EC devices. Both approaches exhibit effective improvement in term of response capability during electrochemical process. Thus, by generating porous structures in the EC polymer films, the response time can be reduced obviously due to the easier diffusion through the EC polymer films during electrochemical redox reaction. Consequently, we propose a new concept and try to design and prepare the target polymers with intrinsic microporosity, and expect the obtained polymer could improve the EC behaviors more effectively and directly.

A Facile Synthesis of Redox-active Polymers with Intrinsic Microporosity for Enhancing Electrochromic Behaviors

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Pressure-Induced Variations in Luminescence Properties of Polyimides having Fluorescent End-groups Exhibiting Excited-State Intramolecular Proton Transfer

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Introduction: Polyimides (PIs) are known as high-performance engineering plastics exhibiting high thermal and chemical stability, mechanical strength, and good flexibility. PIs having fluorescent end-groups exhibiting excited-state intramolecular proton transfer (ESIPT) ability have been attracted lots of interests owing to their prominent fluorescence with large Stokes shifts^[1]. On the other hands, the fluorescent properties of PIs significantly depend on not only the primary structures but also the molecular aggregated state. Recently, we reported that the intensity of main-chain fluorescence in PIs decreased at higher pressures due to enhanced nonradiative deactivations facilitated by intermolecular energy transfer^[2]. In this study, correlation between the aggregated state and the fluorescent properties in PIs having end-groups displaying ESIPT fluorescence was examined based on emission spectra under high pressure.

Experimental & methods: The chemical structures of the target end-capped PIs, sBPDA/DCHM-3HPA (sBPDC-3HPA) and 6FDC/DCHM-3HPA (6FDC-3HPA), are shown in **Fig. 1**. To generate high pressure, PI films were loaded into a sample chamber of diamond anvil cell (DAC, Syntech Co. Ltd.) (**Fig. 2**). The ruby fluorescence technique was used to measure the pressure inside sample chamber. The photoluminescence spectra of the PI films at high pressures (from 0.1 MPa to 2.0 GPa) were measured by a multichannel CCD spectrometer (Hamamatsu Photonics), and a LED light ($\lambda_{\text{ex}} = 365 \text{ nm}$, Hamamatsu Photonics) was used as an excitation light source.

Results and discussions: The intensity of the fluorescent peak observed at 550 nm, assignable to the keto form of the end-groups of sBPDC-3HPA, significantly decreased with increasing the pressure. This is explainable by the enhancement of intermolecular energy transfer accompanied by a decrease in the main-chain / end-groups distance. (**Fig.3(a)**). On the other hand, the intensity of end-group fluorescence of 6FDC-3HPA at 550 nm obviously increased at elevated pressures (**Fig.3(b)**). In this case, energy transfer between the main-chain and end-groups was suppressed because of the lower optical absorbance of 6FDC units. Thereby, the increase in fluorescence is attributable to the suppression of local molecular motion by pressure. These results clearly indicate that the restraint of intermolecular energy transfer in PIs having fluorescent end-groups is a key factor to develop novel luminescent materials which show outstanding fluorescence properties even in densely aggregated states.

Reference: [1] K. Kanosue, S. Ando, et al., *Macromolecules*, **48**, 1777 (2015). *ibid.* **49**, 1848 (2016).

[2] K. Takizawa, S. Ando et. al, *Macromolecules*, **44**, 49 (2011). *ibid.* **47**, 3951 (2014).

Pressure-Induced Variations in Luminescence Properties of Polyimides having Fluorescent End-groups Exhibiting Excited-State Intramolecular Proton Transfer

Koichiro MUTO¹, Eisuke FUJIWARA¹, Ryohei ISHIGE¹ and Shinji ANDO¹ (¹Dept. Chem. Sci. Eng., Tokyo Institute of Technology, E4-5, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, JAPAN) Tel: +81-3-5734-2889, Fax: +81-3-5734-2889, E-mail: kmuto@polymer.titech.ac.jp

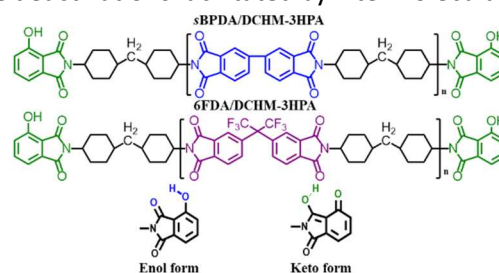


Fig. 1 Chemical structures of end-capped PIs.

• Diamond anvil cell

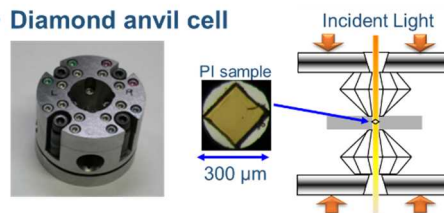


Fig. 2 Photo image of DAC and schematic illustration of the cross section

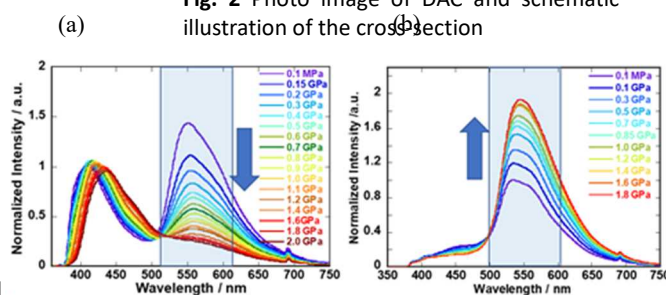


Fig. 3 Variations in emission spectra of (a) sBPDC-3HPA and (b) 6FDC-3HPA by applying pressure up to 2.0 GPa

27th Jappan Polyimide & Aromatic Polymers

Conference Program (15th Nov 2019) (*Tentative*)

Date: **15th, November 2019** (Fri) 10:00~19:00

Venue : Tokyo Institute of Technology, Ookayama
Kuramae-Hall (Large Conference Room)

- 9:30~ Registration
- 10:00~ Opening S. Ando, R. Yokota
- 10:05~ **Mitsuru Ueda** (TokyoTech, Japan)
"Advances in Polycondensation Polymer Synthesis"
- 10:45~ **Guey-Sheng Liou** (Nat. Taiwan Univ., Taiwan)
"New Trends of High-Performance Polymers for Advanced Applications"
- 11:15~ **Jianhua Fang** (Shanghai Jiao Tong Univ., China)
"Synthesis and Fuel cell Performance of Sulfonated Polyimide Multiblock Copolymer Membranes"
- 11:45~ Lunch Time
- 12:45~ Student Poster Presentations, Odd number
- 13:25~ Student Poster Presentations, Even number
- 14:15~ **Kohei Goto** (Goto Engineering Consultant Office, Japan)
"Development Trends of Transparent Flexible Polyimides"
- 14:40~ **Junko Morikawa** (TokyoTech, Japan)
"Verification of Thermophysical Property by Ultrafast Thermal Analysis and Design of Thermally Conductive Polymers by Machine Learning"
- 15:05~ **Yu SHOJI** (Toray Industries, Japan)
"Elucidation of Reaction and Adhesion State of Polyimide-Copper Interface"
- 15:25~ **Kazuya Matsumoto** (Akita Univ., Japan)
"Synthesis of Highly Heat-resistant Aromatic Polyketone by Non-equimolar Polycondensation"
- 15:55~ **Yasushi Nishikawa** (Kaneka Corporation, Japan)
"Thermal Degradation of Polyimides and Thermally Conductive Graphite Sheets"
- 16:20~ **Jun-ichi Isii** (Toho Univ., Japan)
"Function Improvement Effect of Polyimides using Special Monomers"
- 16:45~ **Akira Takahashi** (Kanagawa Univ., Japan)
"Photo-Fries Rearrangement and Refractive Index Change in Aromatic Polyurethane Backbone"
- 17:05~ Closing
- 17:20~ **Banquet + Student Presentation Awards**
- 17:30~19:00 **Company and Voluntary Student Poster Presentation**