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学位論文題目	Poly(phenylisocyanide)s with Controlled Structures and Functions (ポリフェニルイソシアニドの構造制御による機能開拓)			
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Summary

A rod-rod diblock copolymer polythiophene-block-poly(phenylisocyanide) (PTh-*b*-PPI), composed of a π -conjugated polymer and a rod-type helical coiled polymer using the reported methodology was prepared. Introduction of PPI block in the block copolymer architecture enabled PTh-*b*-PPI film to exhibit solid-to-liquid crystal phase transition by exposure to chloroform vapor, accompanied with color change (purple-to-yellow), which is the first report on a new phenomenon of “vapor-induced liquid crystallinity”. Macroscopic orientation of polymer film was achieved using high-intensity magnetic field. In addition, PTh-*b*-PPI film showed color change (purple-to-vermillion) during mechanical shearing, and spontaneously recovered under ambient conditions. Synthesis of a series of polythiophene derivatives and investigation of the properties of the corresponding block copolymers were carried out. Each block copolymer exhibits lyotropic liquid crystallinity and solvent-induced color changes. From grazing-incident X-ray diffraction (GIXRD) measurements for the films, incorporation of rod-shaped PPI block induces the liquid crystalline-like structure in solid state. Polarizing optical microscopy (POM) observations for drop-cast poly1-*b*-PPI copolymer films also showed that lyotropic LC formation was dependent on the molecular weight of PPI (rod-shaped polymer) block. We noticed that grain size (LC domain) of the polymer assembly increased as the molecular weight of PPI block increased. These results suggest that the aspect-ratio of PPI block is a key factor for the block copolymer to show LC phase. Introduction of PPI block to the semiconducting polymer block allow the corresponding block copolymer to show moderate magnetic anisotropy and grain size enough

for magnetic orientation.

Functional block polymers were prepared by introduction of mesogenic moiety in the side chain of PPIs using living polymerization from poly(3-ocylthiophene) (P3OT) macro-initiator. As azobenzene (Azo) moiety possess photo-isomerization property, P3OT-*b*-PPIazo exhibits UV-induced *trans-cis* isomerization and visible light-induced *cis-trans* isomerization in THF solution. P3OT-*b*-PPIazo with long PPI block ($M_n = 74.1\text{ kDa}$, $M_w/M_n = 1.09$, P3OT:PPIazo = 8:92) exhibits lyotropic liquid crystal in THF concentrated solution. Utilizing vapor-induced liquid crystalline nature of P3OT-*b*-PPIazo, several orientation methods are applicable like gentle-shear stress and magnetic field-assisted unidirectional orientations. P3OT-*b*-PPIazo is dissolved in hot cyclohexane, which is selective solvent for PPIazo block, and subsequent cooling to room temperature leads to micro-sized sheet formation. This phenomenon is probably related to crystallization-driven self-assembly (CDSA) of “core-forming” semi-crystalline P3OT block and “corona-forming” PPIazo block in cyclohexane. Cyanobiphenyl (CB) moiety incorporated P3OT-*b*-PPIcb ($M_n = 16.6\text{ kDa}$, $M_w/M_n = 1.50$) shows colloid-forming property in THF(0.04 mg/mL) because of poor solubility of CB moiety. As P3OT block possess semiconducting nature, P3OT-*b*-PPIcb colloid exhibits redox-activity by solution doping with I_2 (oxidant) and hydrazine (reductant). GIXRD measurement for the solid film shows high order of P3OT-*b*-PPIcb film, which is probably derived from CB moiety-incorporated PPIcb block.

The solution drying method to prepare the C_{60} crystals in the presence of PPI was employed and systematically investigated the effects of molecular weights (aspect ratio of PPIs), side chains of PPIs, and weight ratios of C_{60} to PPIs on the C_{60} crystallization. Using optical microscopy, atomic force microscopy (AFM), GIXRD, and scanning electron microscopy (SEM), demonstrating high-aspect-ratio PPIs with non-branched alkyl side chains facilitated 1D crystallization of C_{60} into ultralong whiskers and fibers exceeding 1 mm (up to 3 mm), which were phase separated from PPI and solvent molecules. Furthermore, using living polymerized PPIs we found that higher molecular weight of PPI (higher aspect ratio of rod-shape) afforded longer C_{60} 1D assemblies. The “rod-shaped polymer-controlled crystallization” concept was applicable to other small organic molecules, fullerene C_{70} , tetraphenylethylene, 5,6,11,12-tetraphenylnaphthacene, and tetraphenylporphyrin, to afford 1D molecular assemblies such as elongated whiskers, fibers, and dendritic structures.

New achiral *ortho*-methyl substituted phenylisocyanide monomer structure was designed. Using *o*-tolyl(dppe)NiCl as catalyst allowed synthesis of well-controlled molecular weight PPIs with narrow polydispersity ($M_w/M_n \sim 1.10$) in moderate yield in cholesteric liquid crystal medium at rt. The as-prepared PPI exhibits Cotton effect around 365 nm in circular dichroism (CD) spectrum derived from helical arrangement of imino moiety ($n-\pi^*$ transition). The CD result indicates PPI prepared in cholesteric liquid crystal (CLC) form preferentially one-handed helical backbones. Moreover, ^{13}C NMR for PPIs prepared in CLC suggests the high stereo-regularity of PPI main chains.

[Comment]

The Dr thesis by Hiroki Hayashi discusses synthesis of a series of block copolymer consisting of poly(phenylisocyanide)s and polythiophene derivatives, vapor-induced polymer liquid crystal, photo-isomerization, synthesis of ultra long C₆₀ crystal fiber, and living polymerization in liquid crystal medium. These contents are original idea of Hayashi. Especially, living polymerization with optical activity is a first example in the world. He synthesized the longest C₆₀ crystal wire in the C₆₀ research field using chiral polymer guide. Electron microscopy, atomic force microscopy, and synchrotron XRD measurement technique are combined for characterization of properties of the polymers thus synthesized. Highly synthetic technique in the experiments and the latest measurement methods used in this study allow production and evaluation of new functional polymers. This thesis contains polymer synthesis (living polymerization), liquid crystal, and crystal technology as an excellent piece of work.

[Final Examination result]

The final examination committee conducted a meeting as a final examination on 15 February, 2019. The applicant provided an overview of dissertation, addressed questions and comments raised during Q&A session. All of the committee members reached a final decision that the applicant has passed the final examination.

[Conclusion]

Based on the results of the above-mentioned dissertation defense and final examination, the final examination committee approved that the applicant is qualified to be awarded Doctor of Philosophy in Engineering.