

Division of Materials Chemistry – Chemistry of Polymer Materials –

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Prof
TSUJII, Yoshinobu
(D Eng)



Assoc Prof
OHNO, Kohji
(D Eng)



Assist Prof
SAKAKIBARA, Keita
(D Agr)



Program-Specific Assist Prof
ISHIGE, Ryohei
(D Eng)



PD
BAEK, Sung Chul
(Ph D)

Researchers(pt)

HSU, Shu-Yao

HUANG, Yun (D Eng)

KAGATA, Hideki (D Environmental Earth Sc)

KAWANO, Yuko

KONISHI, Kyoko

MORIKI, Yoshito

NAKAMICHI, Kimiyo

SAKAUE, Motokazu

SEO, Haruna

Students

NAKANISHI, Yohei (D3)

YAHATA, Yoshikazu (D2)

AKIMOTO, Shuhei (M2)

KINOSE, Yuji (M2)

SHIKURI, Ryuji (M2)

TAKAHASHI, Kenichi (M2)

NOGAMI, Naotsugu (M1)

MASUDA, Shota (M1)

WADA, Ryota (M1)

ZHAO, Chenzhou (RS)

ISHIBASHI, Daigo (UG)

EGI, Kohki (UG)

YAMASHITA, Kohei (UG)

Guest Research Associates

EJAZ, Muhammad (D Eng)

Tulane University, U.S.A., 10 July–9 September

IOCOZZIA, James Arthur

Georgia Institute of Technology, U.S.A., 17 June–19 August

Scope of Research

Kinetic and mechanistic analyses are made for better understandings of the chemical and physicochemical reactions occurring in polymerization systems and for better routes to the synthesis of well-defined polymers. By various polymerization techniques, in particular, living polymerizations, new well-defined polymers or polymer assemblies are prepared, and their structure/properties relationships are precisely analyzed. Projects in progress include: (1) Kinetics and mechanisms of living radical polymerization (LRP). (2) Synthesis of new polymeric materials by living polymerizations and their structure/properties studies. (3) Synthesis, properties, and applications of concentrated polymer brushes (CPB).

KEYWORDS

Precision Polymerization

Living Radical Polymerization

Hybrid Materials

Biointerface

Polymer Brush



Selected Publications

Tsujii, Y.; Nomura, Y.; Okayasu, K.; Gao, W.; Ohno, K.; Fukuda, T., AFM Studies on Microtribology of Concentrated Polymer Brushes in Solvents, *J. Phys.: Conf. Ser.*, **184**, no. 012031 (2009).

Arita, T.; Kayama, Y.; Ohno, K.; Tsujii, Y.; Fukuda, T., High-Pressure Atom Transfer Radical Polymerization of Methyl Methacrylate for Well-Defined Ultrahigh Molecular-Weight Polymers, *Polymer*, **49**, 2426-2429 (2008).

Tsujii, Y.; Ohno, K.; Yamamoto, S.; Goto, A.; Fukuda, T., Structure and Properties of High-Density Polymer Brushes Prepared by Surface-Initiated Living Radical Polymerization, *Adv. Polym. Sci.*, **197**, 1-45 (2006).

Ohno, K.; Morinaga, T.; Takeno, S.; Tsujii, Y.; Fukuda, T., Suspension of Silica Particles Grafted with Concentrated Polymer Brush: Effects of Graft Chain Length on Brush Layer Thickness and Colloidal Crystallization, *Macromolecules*, **40**, 9143-9150 (2007).

Ohno, K.; Morinaga, T.; Koh, K.; Tsujii, Y.; Fukuda, T., Synthesis of Monodisperse Silica Particles Coated with Well-Defined, High-Density Polymer Brushes by Surface-Initiated Atom Transfer Radical Polymerization, *Macromolecules*, **38**, 2137-2147 (2005).

Controlled Synthesis of High-molecular-weight Triblock Copolymers and Their Gel Formation in Ionic Liquid

Well-defined and high-molecular-weight triblock copolymers containing poly(styrene) (PS) and poly(methyl methacrylate) (PMMA) as A- and B-segments, respectively, were prepared by atom transfer radical polymerization techniques using a bi-functional initiator under a high pressure and/or in an ionic-liquid solvent. The optimization of polymerization conditions enabled us to achieve a block efficiency higher than 90% and a total molecular weight over one million. The triblock copolymer efficiently gelled an ionic liquid, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI), which is a good solvent for PMMA but a non-solvent for PS, even at a concentration as low as 0.5 wt% simply by casting using volatile solvent. Thus obtained gels were rheologically and electrochemically characterized, demonstrating a conductivity as high as 0.1 mS/cm at a polymer concentration of 10 wt %. The structure of cross-linking point, as was expected to be a microphase-separated domain of PS, was dependent especially on the molecular weight of PS block. The figure compares two samples with almost the same molecular weight of PMMA but different molecular weights of PS. Interestingly, the sample of higher molecular weight PS gave a blue color, that is a kind of structural colors. The SAXS measurement estimated the size and its distribution of PS domain to be 21.4 nm in R_0 and 1.7 in standard deviation. The correlation between PS domains is still under investigation.

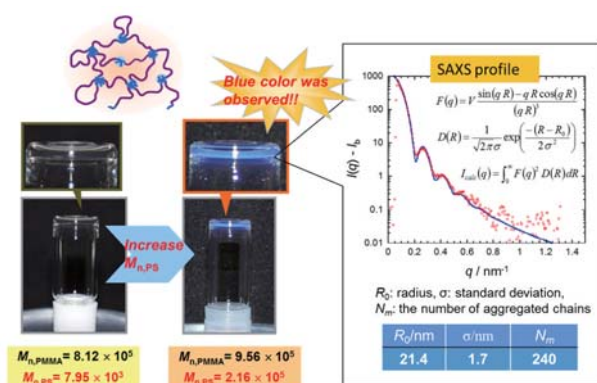


Figure 1. Gelation of ionic liquid by ABA-triblock copolymers and SAXS profile determining the structure of crosslinking PS-domain.

Design of Diblock Copolymer Dispersants for Cellulose Nanofiber Reinforced Resin Nanocomposite Materials

Among mechanically strong and lightweight materials, cellulose nanofibers (CNFs) have a range of promising properties leading to fiber-reinforced thermoplastic composites. Owing to the hydrophilic nature on surface, CNFs can only be stable in the form of aqueous suspensions and are compatible with hydrophilic resins, so that the development of CNF-reinforced hydrophobic matrices such as polyolefin is most challenging. One of promising strategies is the modification of CNF surface to make it hydrophobic. We have successfully fabricated CNF-reinforced nanocomposite materials of high-density polyethylene (HDPE) using a diblock copolymer as a dispersant, which relies on the multiple and concerted interaction via strong hydrogen bonding between a cellulose-interactive segment of the block copolymer and CNF surface (Figure 2a). In fact, simple addition of a designed block copolymer resulted in much reduced aggregation of CNFs in HDPE matrices (Figure 2b) and hence significant increase in Young's modulus (over twice) and tensile strength (about 1.5 times) (Figure 2c). This study represents a potential approach to mediate CNF-CNF and CNF-resin interactions and to significantly improve the dispersibility of CNF without chemical functionalization, which can be a low-cost and environmentally green process especially suitable for an industrial application.

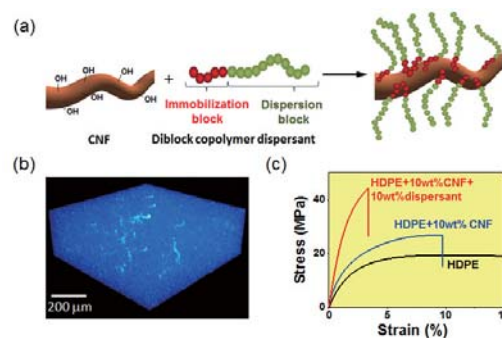


Figure 2. (a) Schematic illustration of adsorption of polymer dispersant onto cellulose nanofiber (CNF). (b) Reconstructed 3D X-ray CT image of CNF-reinforced HDPE nanocomposite with dispersant. (c) Representative stress-strain curves.