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– Chemistry of Polymer Materials –

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Scope of Research

We perform kinetic and mechanistic analyses toward understanding chemical and physicochemical reactions occurring in polymerization systems and better routes for synthesis of well-defined polymers. In particular, new well-defined polymers or polymer assemblies are prepared by living polymerization techniques, 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; and 3) synthesis, properties, and applications of concentrated polymer brushes (CPB).

KEYWORDS

Precision Polymerization
Living Radical Polymerization
Polymer Brush
Tribology
Hybrid Materials

Recent Selected Publications

Nakanishi, Y.; Ishige, R.; Ogawa, H.; Huang, Y.; Sakakibara, K.; Ohno, K.; Kanaya, T.; Takenaka, M.; Tsujii, Y., Unified Explanation for Self-Assembly of Polymer-Brush-Modified Nanoparticles in Ionic Liquids, *Polymer Journal*, **55,** 1199-1209 (2023).

Okubo, H.; Kagiwata, D.; Sasaki, S.; Tsujii, Y.; Nakano, K., Operando Tribo-Raman Spectroscopic Observation for Wear Processes of Superlow Frictional Concentrated Polymer Brushes at Frictional Interface, *Polymer Testing*, **127,** 108170 (2023).

Ishida, K.; Kondo, T., Evaluation of Surface Free Energy Inducing Interfacial Adhesion of Amphiphilic Cellulose Nanofibrils, *Biomacromolecules*, **24,** 3786-3793 (2023).

Sakakibara, K.; Tsujii, Y., Visualization of Fibrillated Cellulose in Polymer Composites Using a Fluorescent-Labeled Polymer Dispersant, *ACS Sustainable Chemistry and Engineering*, **11,** 9332-6342 (2023).

Ishida, K.; Kondo, T., Anisotropic Frictional Properties Induced by Cellulose Nanofibril Assembly, *Biomacromolecules*, **24,** 3009-3015 (2023).

Precision Synthesis of Asymmetric Cellulose Nanocrystals with Regioselectively End-Grafted Polymer Brushes

The cellulose nanocrystal (CNC), which is a nanoparticle obtained by hydrolysis of cellulose, has many intriguing properties, including strength, stiffness, biocompatibility, biodegradability, and high aspect ratio. Notably, recent advancements have been made in selectively modifying aldehyde groups located at the reducing edge of CNC with end-grafted polymer chains. Nanoparticles with high-density, concentrated polymer brush (CPB) can form colloidal crystals because of the high resistance against compression and the extremely low friction of the CPB layer. Therefore, we hypothesized that the CNC, with two types of polymers (of different molecular weights) regioselectivity grafted on its reducing edge and other sides (referred to as an asymmetric polymer-brush-modified nanorod: asym-PB nanorod, **Fig. 1**), could form novel higher-order structures because of its asymmetric shape and interparticle repulsive potential.

In this study, we have developed a novel synthetic route for asym-PB nanorods. This involves the introduction of azido groups to the reducing edge of CNC followed by the click reaction to couple reversible addition-fragmentation chain transfer (RAFT) polymerization initiators. Subsequently, atom transfer radical polymerization (ATRP) initiators were introduced to hydroxyl groups on the CNC-side surface to yield a CNC macroinitiator (**Fig. 1**). Finally, successive RAFT polymerization and ATRP were conducted to obtain the desired asym-PB nanorod. We have confirmed that thus obtained asym-PB nanorod had densely grafted polymer chains at the reducing edge and other CNC-side surface through various evaluations. The surface pressure–area per molecule (π–A) isotherms of the asym-PB nanorod showed a distinctive plateau (**Fig. 2**), suggesting a phase transition occurring possibly thanks to the polymer brush of high molecular weight at the reducing edge. The details studies are now in progress, and our ultimate objective is to create a novel higher-order structure of asym-PB nanorods.

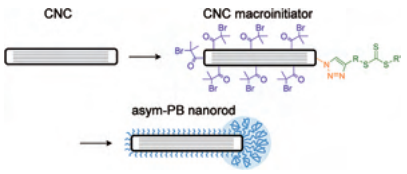

Figure 1. Synthetic scheme for asym-PB nanorod.

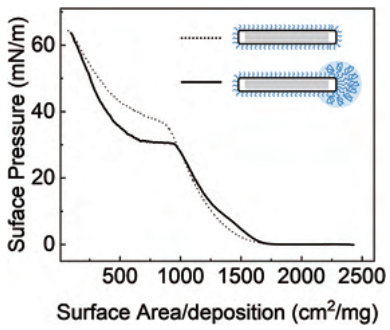

Figure 2. π–A curves for asym-PB nanorod and its analogue.

Hydration Water and Anti-Icing Functions of Hydrophilic Concentrated Polymer Brushes

Hydrophilic concentrated polymer brushes (CPBs) are expected to exhibit antifouling, antifogging, and anti-icing functions, which have been actively studied. To comprehensively understand the mechanism of these functions, it is essential to understand the interaction between CPB and water. However, there are only a few studies on direct measurement of such interactions, and in particular, its analysis and observation at low temperatures, which are important for elucidating the mechanism of the anti-icing property, have not yet been accomplished. One of the reasons for this is that CPB is usually an ultra-thin film, making it difficult to apply general-purpose analytical methods. Recently, we succeeded in synthesizing hydrophilic CPBs that are an order of magnitude thicker than previously possible. In this study, we have challenged to directly observe the hydration state of water inside CPB, which had never been achieved before, using CPBs with an ultra-large thickness as the key materials. The results are discussed in relation to the anti-icing property at the CPB interface.

Through the atom transfer radical polymerization of poly (ethylene glycol) methyl ether methacrylate (PEGMA) as a monomer, a hydrophilic CPB with a thickness of about 1 μm was synthesized on a Si wafer. The ice adhesion strength was measured by horizontally peeling off a cylndrical ice pillar prepared on a surface-modified Si wafer in a temperature-controlled microscopic stage. The results are shown in **Fig. 3**, suggesting that the effect was above the icephobic level, which is based on 100 kPa or lower. In addition, the hydration state of water-swollen CPB was analyzed by infrared microspectrometry (**Fig. 4**). It was observed that water inside the brush does not freeze even at low temperatures, and this is considered to be responsible for the excellent anti-icing function. Further investigation is currently on-going.

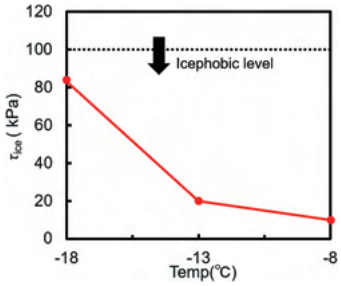

Figure 3. Temperature dependency of ice adhesion strength τ_{ice} for CPB.

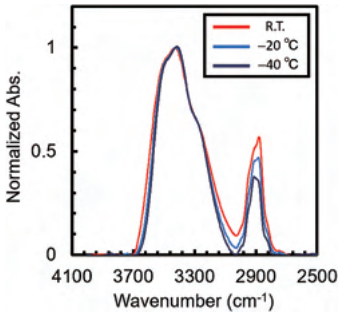

Figure 4. IR spectra of the water-containing PPEGMA-CPB at positions near a water droplet as a function of temperature.