Division of Materials Chemistry
– 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
Polymer Brush
Biointerface
Living Radical Polymerization
Hybrid Materials

Selected Publications

Hsu, S.-Y.; Kayama, Y.; Ohno, K.; Sakakibara, K.; Fukuda, T.; Tsujii, Y., Controlled Synthesis of Concentrated Polymer Brushes with Ultralarge Thickness by Surface-Initiated Atom Transfer Radical Polymerization under High Pressure, *Macromolecules*, **53,** 132-137 (2020).

Sakakibara, K.; Wakiuchi, A.; Murata, Y.; Tsujii, Y., Precise Synthesis of Double-armed Polymers with Fullerene C_{60} at the Junction for Controlled Architecture, *Polym. Chem.*, **11,** 4417-4425 (2020).

Tadokoro, C.; Sato, K.; Nagamine, T.; Nakano, K.; Sasaki, S.; Sato, T.; Sakakibara, K.; Tsujii, Y., Concentrated Polymer Brush as Reciprocating Seal Material for Low Leakage and Low Friction, *Tribology Transactions*, **63,** 20-27 (2020).

Hsu, S.-Y.; Ohno, K.; Sakakibara, K.; Tsujii, Y., Convenient Synthesis of Very-Thick Concentrated Polymer Brushes by Atom Transfer Radical Polymerization in an Ionic Liquid, *Macromolecules*, **53,** 7936-7943 (2020).

Sakakibara, K.; Moriki, Y.; Tsujii, Y., Simultaneous Nanofibrillation and Compounding of Wood Pulp Fibers Using Polyols as Plasticizers: Fabricating High-performance Cellulose-nanofiber-reinforced Polyethylene Composites, *J. Fiber Sci. Technol.*, **76,** 23-31 (2020).

Elasto-hydrodynamic Lubrication on Well-defined, Epoxy-Resin-Based Monolith Containing Ionic Liquid

We have successfully realized an elasto-hydrodynamic lubrication (EHL) on a monolithic thin film of well-defined, bicontinuous three-dimensional networks of polymer framework and pore, which is prepared through polymerization-induced phase separation in the presence of a non-reactive porogen. In the EHL as one of hydrodynamic lubrication mechanisms, the friction and wear can be reduced by significant elastic deformation of the surface and hence effective formation of lubricant layer between the rubbing (base) materials (inhibiting the direct contact). **Figure 1** schematically illustrates the experimental setup: the monolith surface was sputter-coated by aluminium to enhance the reflectivity, and the probe-glass lens was modified with a 480-nm silicate layer on a reflective Cr one to precisely determine a small thickness. **Figure 2** shows the measured film thickness h_c of the lubricant (poly-α-olefin, viscosity = 110 cP at 25 °C) as a function of sliding velocity v. In an immersed condition, the h_c value decreased with decreasing v with a slope of 0.58 in this plot, which is almost consistent with the EHL theory. It is surprising that the EHL mechanism was kept even at a lubricant-layer thickness of ~ 10 nm, much smaller than the surface roughness of the probe lens. Another important point is that even in a so-called "starved" condition, similar lubrication was achieved in a relatively low velocity. These tribological properties characteristic to the monolith materials is well understood from the viewpoint of the deformation of the polymer framework and the hydrodynamic effect of thus excluded lubricant. This monolith-coating system is expected to be applicable on various mechanical elements for their prolonged life and energy saving.

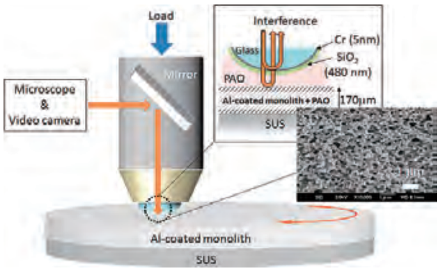

Figure 1. Schematic illustration of in-situ frictional/optical measurements in ball-on-disk setup.

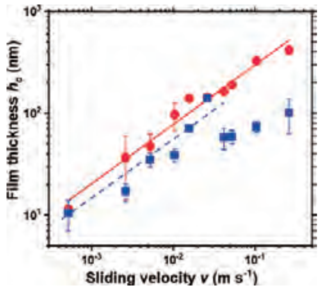

Figure 2. Double logarithmic plot of lubricant-film thickness h_c at a normal load of 1N against sliding velocity v in immersed (●) and starved (■) lubrication conditions using PAO as a lubricant.

Controlling the Thermally Induced Phase Separation of Polymer/Ionic-Liquid Blended Films with Concentrated-Polymer-Brush-Decorated Hybrid Particles

The development of quasi-solid electrolytes for electrical devices operating at high voltages is important to address future energy storage requirements. Here, we report a new method to fabricate quasi-solid electrolytes through the thermally induced phase separation of a polymer/ionic-liquid (polymer/IL) blend. In a polymer/IL blend that exhibits lower critical solution temperature-type phase separation, we demonstrate that the addition of silica particles decorated with concentrated polymer brush (CPB-SiPs) can prevent the macroscopic phase separation after heating, resulting in a quasi-solid electrolyte with a continuous IL phase. This is due to the adsorption of CPB-SiPs onto the polymer/IL interface in the phase-separated structure. We also reveal a relationship between the molecular weight of the CPB and the phase-separated structure. Namely, a quasi-solid film with a bicontinuous phase-separated structure is formed only when polymers with an appropriate molecular weight are grafted on the CPB-SiPs (**Figure 3**). The resulting quasi-solid film exhibits a relatively high ionic conductivity, owing to the existence of a continuous ion-conductive phase solely consisting of IL. In addition, we fabricated a quasi-solid electrolyte with the blended film and successfully applied it to an electric double-layer capacitor operating at a high voltage, owing to the wider potential window of the IL employed herein.

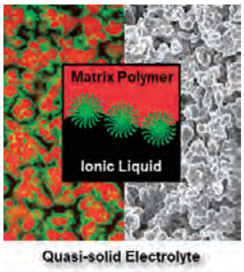

Figure 3. Confocal laser scanning microscopy and scanning electron microscopy images of polymer/ionic liquid blended films added with 10 wt% of polymer-brush-decorated nanoparticles. Red, black, and green correspond to the matrix polymer phase, ionic liquid phase, and nanoparticles, respectively.