# 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
Living Radical Polymerization
Polymer Brush
Hybrid Materials
Biointerface


### 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,** 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).

## Lubrication Properties of Concentrated Polymer Brushes Revealed by Optical Interferometry Method

Fabrication of polymer brushes onto materials is one of attractive methods to modify their surface properties. Especially, polymer brushes with high graft density, which are called as concentrated polymer brushes (CPBs), exhibits various unique features. For example, we have reported the excellent tribological properties of CPBs in their swollen state such as an extremely low friction characteristic, and its potentials as novel tribomaterials so far. In order to obtain further insights into the lubrication and wear mechanisms of CPBs, detailed observations of the contact point under sliding condition should be needed. Herein, we have investigated the tribological properties of CPBs by means of the simultaneous measurements of the film thickness of lubrication layer and friction coefficient, which were determined *in situ* by optical interferometry and tribological sliding test, respectively. The experimental setup of ball-on-disc sliding test is illustrated in Figure 1a. A Newton's ring formed at a contact point of a glass lens and a CPB-fabricated silicon substrate was recorded with a digital microscope, and the gap profile between two surfaces was calculated from this interferogram (Figure 1b and 1c). This experiment was carried out at the sliding speed from 2.8 to 100 mm/s, and as a result hydrodynamically formed lubrication layer was observed at the all of the test conditions. Interestingly, the thickness of this lubrication layer depends on the dry thickness of the CPBs fabricated on the substrate, which suggested that CPBs plays a critical role to realize an extremely low lubrication surface. Detailed lubrication mechanisms are currently being investigated by using other analytical methods such as an atomic force microscopy and a rheological measurement.

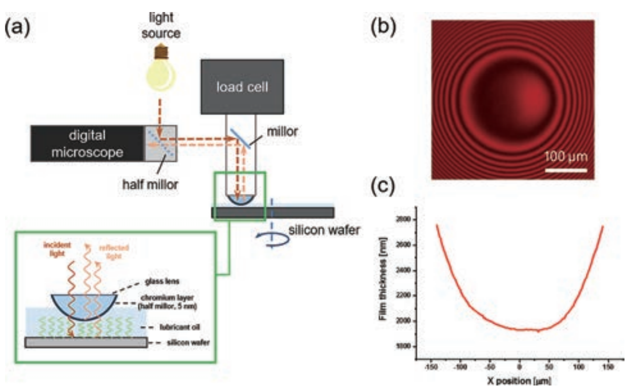


**Figure 1.** (a) Schematic diagram of an experimental set-up. (b) A photo image of the Newton's ring formed at the contact point. (c) A gap profile between a lens and a CPB-fabricated silicon substrate.

## Versatile Preparation of Surface-Skinless Particles of Epoxy Resin-Based Monoliths Using a Well-Defined Diblock Copolymer Surfactant

Epoxy resin-based monoliths, possessing bicontinuous structure that consists of a porous channel and a resin skeleton, have a broad range of applications such as chromatography; however, the preparation of spherical particles has been limited so far. This is the first report on a versatile and facile preparation method for surface-skinless monolithic particles with micrometer diameters by polymerization-induced phase separation in an oil-in-oil emulsion system (Figure 2). The key to success was the addition of a well-defined block copolymer surfactant, compatible for both the dispersed and continuous phases in suspension polymerization. In essence, the volume ratio and length of the block copolymers were crucial to controlling the stability of emulsion and the suppression of the unwanted skin layer on the surface of the produced particles. The surface-skinless monolithic particles could be further applied to flow-through particles, which are promising for chromatography and preparative applications. The present work thus represents a new direction for versatile and large-scale preparation of monolithic particles, including silicates and polyacrylates, with several surface properties.

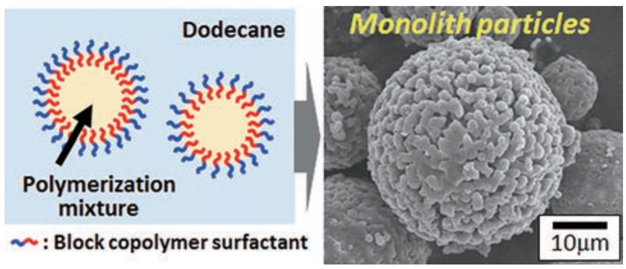


**Figure 2.** Preparation of epoxy resin-based monolithic particles.