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
Tribology
Hybrid Materials

Recent Selected Publications

Nakanishi, Y.; Sakakibara, K.; Nakamichi, K.; Ohno, K.; Morinaga, T.; Sato, T.; Sagawa, T.; Tsujii, Y., Concentrated-Polymer-Brush-Modified Silica Nanoparticles Self-Assembled in Ionic Liquid Containing Iodide/Triiodide (I^-/I_3^-)-Redox System as Quasi-Solid Electrolytes for Dye-Sensitized Solar Cells, *ACS Appllied Nano Materials*, **4,** 6620-6628 (2021).

Sakakibara, K.; Ishida, H.; Kinose, Y.; Tsujii, Y., Regioselective Synthesis of Cellulosic Janus Bottlebrushes with Polystyrene and Poly (ε-Caprolactone) Side Chains and Their Solid-State Microphase Separation, *Cellulose*, **28,** 6857-6868 (2021).

Kinose, Y.; Sakakibara, K.; Sato, O.; Tsujii, Y., Near-Zero Azimuthal Anchoring of Liquid Crystals Assisted by Viscoelastic Bottlebrush Polymers, *ACS Appl. Mater.*, **3,** 2618-2625 (2021).

Sakakibara, K.; Maeda, K.; Yoshikawa, C.; Tsujii, Y., Water Lubricating and Biocompatible Films of Bacterial Cellulose Nanofibers Surface-Modified with Densely Grafted, Concentrated Polymer Brushes, *ACS Appl. Nano Mater.*, **4,** 1503-1511 (2021).

Maguire, S. M.; Krook, N. M.; Kulshreshtha, A.; Bilchak, C. R.; Brosnan, R.; Pana, A.-M.; Rannou, P.; Maréchal, M.; Ohno, K.; Jayaraman, A.; Composto, R. J., Interfacial Compatibilization in Ternary Polymer Nanocomposites: Comparing Theory and Experiments, *Macromolecules.*, **54,** 797-811 (2021).

Study on Shear-Induced Wearing of Swollen Concentrated Polymer Brushes via Fluorescence Detection of Mechanoradicals

The reduction of friction and wear in materials brings to a significant improvement in energy efficiency, product lifetime, and environmental sustainability. As a novel soft material realizing this, a concentrated polymer brush (CPB), an assembly of polymer chains sufficiently densely end-grafted on a solid surface, has received considerable attention. Especially, a thick CPB of a mm-order thickness successfully synthesized by surface-initiated controlled radical polymerization under a high-pressure condition exhibits an excellent low-friction performance in a good solvent even under a macro-scale contact. The key to its social implementation lies in understanding the mechanism of its wearing under severe conditions. In this study, we have developed a novel method to detect chain-scission events of a CPB by trapping thereby generated mechano-radicals with fluorescent monomers and hence observing its wear state using fluorescence microscopy with high sensitivity and resolution. Figs 1 and 2 show an example of fluorescence-microscopic images and its histogram of fluorescence intensity of the CPB layer, which was slid using a glass lens in an ionic liquid containing a fluorescent monomer and then washed with a solvent. We suggest that the obtained wear image can be classified into three regions of different fluorescence intensity and hence different wear state. The area of weak fluorescence intensity was observed almost all along the sliding track, the moderate-intensity area dendritically spread mainly around a defect, and the strong-intensity area was distributed along the sliding direction beyond the moderate-intensity region. Along with the thickness data obtained by a scanning laser microscope, we have discussed the mechanism of CPB wearing especially from the viewpoint of different modes of wear progression toward durability improvement and practical application.

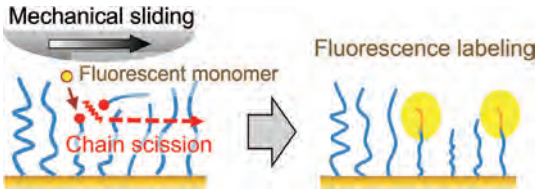

Figure 1. Schematic illustration of CPB wearing by shear force and its fluorescent labeling.

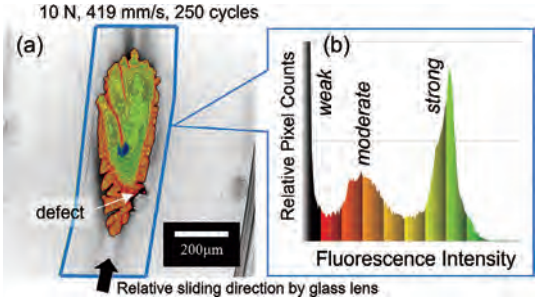

Figure 2. A fluorescence-microscopic image and (b) its histogram of a CPB of poly(methyl methacrylate) worn by mechanical sliding in a lubricant.

Anchoring Property of Liquid Crystal on Bottlebrush Polymer Film Fabricated by Langmuir Blodgett Method

Although liquid crystals (LCs) in bulk can be aligned by external fields such as electric and magnetic fields, the change in the direction of LCs near a surface is restricted by the interaction between LCs and the surface, which is known as the anchoring effect. Previously, it was reported for a bottlebrush comprised of poly(hexyl methacrylate) (PHMA) that LC molecules at the interface of its spin-coated film could easily rotate in the plane according to the external field, which is called the zero-azimuthal anchoring property. In the film fabricated by the spin-coating method, the bottlebrush molecules could be randomly oriented in the film. In this study, we have applied the Langmuir Blodgett (LB) method to control the structure of a film at the molecular level and investigated the anchoring properties of the LB film of the PHMA bottlebrush. The azimuthal anchoring coefficients A_2 on the multilayered LB and spin-coated films was estimated, from the voltage–transmittance curves, to be almost the same (Fig. 3). In contrast, they showed different characteristics in controlling the easy axis of LCs. The LB film maintained an easy axis of LCs perpendicular to the dipping direction even after the studied LC cell was once heated above the nematic-isotropic transition temperature. The alignment-regulating power of the multilayered LB film was stronger than that of the unevenness of a comb electrode (Fig. 4). The reason for this characteristic property of the LB film is discussed from the viewpoints of the orientation of bottlebrush molecules and/or the surface microstructure created during the multilayer-film formation: the detailed mechanism is under investigation.

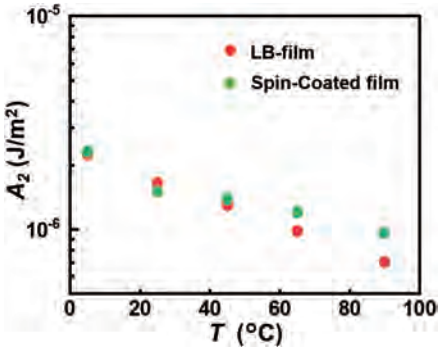

Figure 3. Temperature dependence of A_2 of LB and spin-coated films.

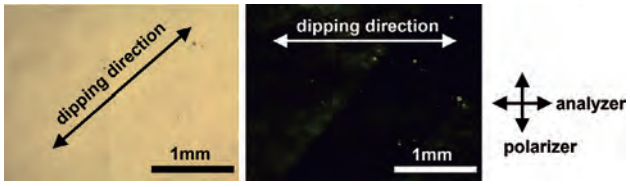

Figure 4. Polarization-microscopic images of LC cell with LB films.