Division of Materials Chemistry
– Chemistry of Polymer Materials –

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Mr FERRIER, Robert University of Pennsylvania, U.S.A., 19 June–21 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
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,** 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).

Novel Tribomaterials of Cellulosic-Nanofiber Sheets with Well-Defined Bottle-Brushes

Previously, we developed a novel graft-type of gels, i.e., a gel of cross-linked bottle brushes, having an excellent-lubricating property. The key to success was to keep the side-chain length short enough to achieve the CPB effects (including super lubrication) originating from the highly stretched-chain conformation and high-density segmental density in a solvent, where CPB represents the concentrated polymer brush (successfully and systematically synthesized by controlled radical polymerization techniques). In order to further improve the mechanical property, we have attempted to reinforce it by nano-fibers; in brief, the bacteria-producing hydrogel containing cellulosic nanofibers (CNF) was hot-pressed into a non-woven sheet with an excellent mechanical strength, which was filled up with bottle brushes of short side chains of poly(styrene) (PS). Figure 1 shows the scanning electron micrographs on the surface of the CNF sheet before and after incorporating the bottle brush, suggesting the well-defined, higher-order structure. The frictional property was measured in toluene, a good solvent for PS, on the surfaces of the composite as well as original CNF sheets. Figure 1 plots the frictional coefficient μ as a function of shear velocity v, clearly suggesting that the filling with the bottle brush much improves the lubricating property. Similar structure can be found in the articular cartilage of a human joint, but the difference is the mechanism for lubrication, that is the electrostatic interaction of charged groups but not the CPB effect. We believe that this study will open up a new route to novel tribomaterials on the based on the CPB concept.

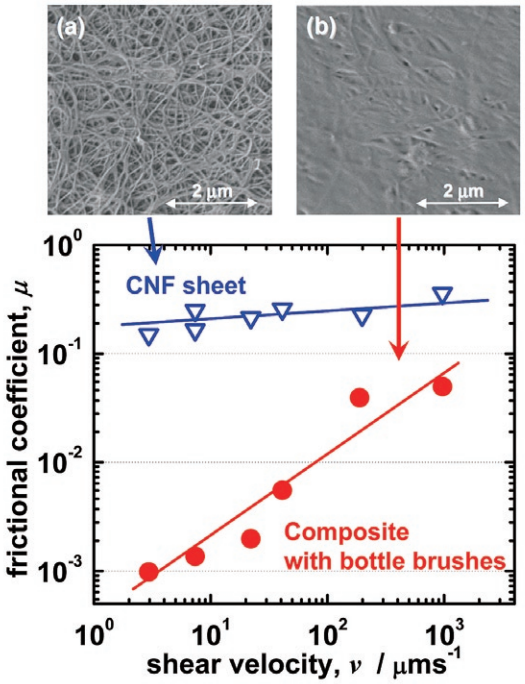

Figure 1. SEM images (a, b) and frictional property (plot of μ vs v in toluene) on the surfaces of the CNF sheets with and without bottle brushes insides.

Blood Clearance and Biodistribution of Polymer Brush-Afforded Silica Particles Prepared by Surface-Initiated Living Radical Polymerization

The physiological properties of polymer brush-afforded silica particles prepared by surface-initiated living radical polymerization were investigated in terms of the circulation lifetime in the blood and distribution in tissues. A series of hybrid particles were synthesized by varying the diameter of the silica core and the chain length of the polymer brush in order to examine the relationship between their physicochemical and physiological properties. The hybrid particles were injected intravenously into mice to systematically investigate their blood clearance and body distribution. It was revealed that the structural features of the hybrid particles significantly affected their *in vivo* pharmacokinetics. Some hybrid particles exhibited an excellently prolonged circulation lifetime in the blood with a half-life of about 20 h. When such hybrid particles were injected intravenously into a tumor-bearing mouse, they preferentially accumulated in tumor tissue. The tumor-targeted delivery was optically visualized using hybrid particles grafted with fluorescence-labeled polymer brushes.

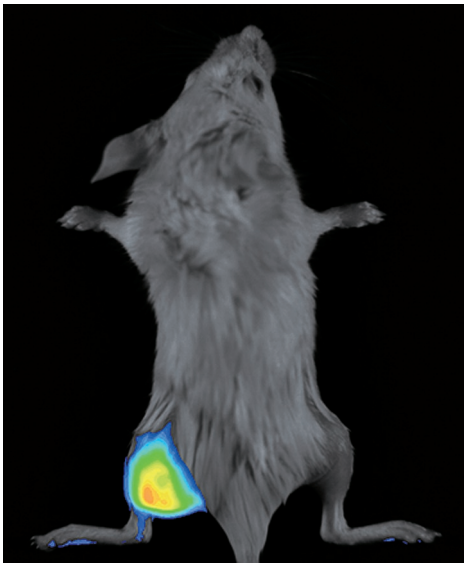

Figure 2. Optical fluorescence image of tumor-bearing mouse taken at 24 h post-injection of hybrid particles grafted with fluorescence-labeled polymer brush.