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– Chemistry of Polymer Materials –

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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).

All-Solid Dye-Sensitized Solar Cell Using Self-Assembled Nanoparticles with High-Density, Concentrated Polymer Brushes

Previously, we succeeded in fabricating a solid membrane of high ionic conductivity using self-assembled nanoparticles with concentrated polymer brushes (CPBs) in an ionic liquid and in developing a novel bipolar-type of lithium-ion rechargeable batteries, where CPB represents the concentrated polymer brush (successfully and systematically synthesized by living radical polymerization techniques). This success was caused by the CPB effects (including super lubrication) originating from the highly stretched-chain conformation and high segmental density in solvent. In this work, we aimed at verifying this concept and expanding it to an iodine/iodide-redox system using poly(DEMM-TFSI) and poly(PEGMA) as a brush component on a nanoparticle. Scanning electron microscopic (SEM) observation and impedance measurement revealed that in a redox-ionic liquid, a CPB-modified nanoparticle (PSiP) was self-assembled into a solid of a high conductivity for poly (PEGMA) brush but not for poly(DEMM-TFSI) one. These results were understood by the difference in affinity between the brush component and the redox-ionic liquid. Finally, we confirmed the photovoltaic performance of the dye-sensitized solar cell (DSSC) using this new type of PSiP membrane as a novel solid-like electrolyte, in which a continuous channel was constructed in nm scale, being responsible for high ionic conductivity. This work opens up a novel route to non-flammable all-solid type of DSSC.

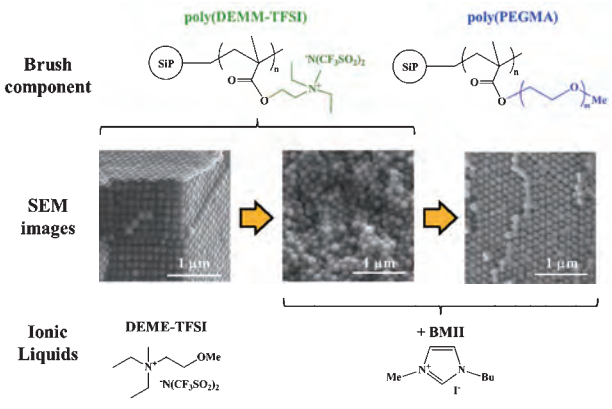

Figure 1. Cross-sectional SEM images of PSiP membranes obtained for different brush/ionic liquid components.

Fabrication of Contrast Agents for Magnetic Resonance Imaging from Polymer-Brush-Afforded Iron Oxide Magnetic Nanoparticles Prepared by Surface-Initiated Living Radical Polymerization

Iron oxide magnetite (Fe_3O_4) nanoparticles were surface-modified using initiating groups for atom transfer radical polymerization (ATRP) via a ligand-exchange reaction in the presence of a triethoxysilane derivative having an ATRP initiation site. The ATRP-initiator-functionalized Fe_3O_4 nanoparticles were used for performing the surface initiated-ATRP of methyl methacrylate. The polymerization proceeded in a living fashion so as to produce graft polymers with targeted molecular weights and narrow molecular weight distribution. The average grafting density was estimated to be as high as 0.7 chains/nm^2, which indicates the formation of so-called concentrated polymer brushes on the Fe_3O_4 nanoparticles. A similar polymerization process was conducted using a hydrophilic monomer, poly (ethylene glycol) methyl ether methacrylate (PEGMA), to prepare Fe_3O_4 nanoparticles grafted with poly(PEGMA) brushes. The blood clearance and bio-distribution of the hybrid particles were investigated by intravenously injecting particles labeled with a radio isotope, ^{125}I, into mice. It was found that some hybrid particles exhibited an excellently prolonged circulation lifetime in the blood with a half-life of about 24 h. When such hybrid particles were injected intravenously into a tumor-bearing mouse, they preferentially accumulated in the tumor tissues owing to the so-called enhanced permeability and retention effect. The tumor-targeted delivery was visualized by a T_2-enhaced magnetic resonance imaging (MRI) measurement.

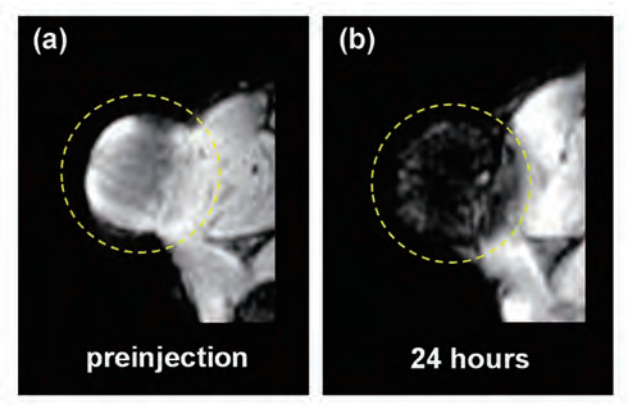

Figure 2. In vivo T_2-weighted magnetic resonance images of a tumor site taken at (a) pre-injection and (b) 24 h post-injection of suspension of PPEGMA-Fe_3O_4 nanoparticles.