

Division of Materials Chemistry – Chemistry of Polymer Materials –

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Mr MORAES, John The University of Sydney, Australia, 1–22 October

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

Nomura, A.; Okayasu, K.; Ohno, K.; Fukuda, T.; Tsujii, Y., Lubrication Mechanism of Concentrated Polymer Brushes in Solvents: Effect of Solvent Quality and Thereby Swelling State, *Macromolecules*, **44**, 5013-5019 (2011).
Sato, T.; Morinaga, T.; Marukane, S.; Narutomi, T.; Igarashi, T.; Kawano, Y.; Ohno, K.; Fukuda, T.; Tsujii, Y., Novel Solid-State Polymer Electrolyte of Colloidal Crystal Decorated with Ionic-Liquid Polymer Brush, *Adv. Mater.*, **23**, 4868-4872 (2011).
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 of Concentrated Polymer Brushes in Ionic Liquids

Ionic liquids (ILs) have been attracting as new type of lubricants especially at high temperatures and/or under vacuum, by their properties of nonvolatility, noncombustibility and wide solvent-temperature ranges. We have investigated lubrication mechanism of concentrated polymer brushes (CPBs) in solvent (Figure 1), which develops super lubrication property affording ultra-low frictional coefficient μ on the order of 10^{-4} . One of the requirements for establishing the super lubrication of CPBs is good solvent condition, in which the brush layers are sufficiently swollen to their fully-stretched grafted chains. Using the ILs as swelling solvents of CPBs attracts us to the further elucidation of lubrication mechanism and designing practical lubricating surface of CPBs. We have recently observed hydrodynamic lubrication feature in the friction of CPBs in ILs, and their μ values were scaled with the viscosities of pure ILs (Figure 2). These results not only enable us to discuss the details of the effect of solvent viscosity on lubrication of the CPBs, but also demonstrate their ability to act as an excellent lubrication system in combination with ILs as lubricating fluids.

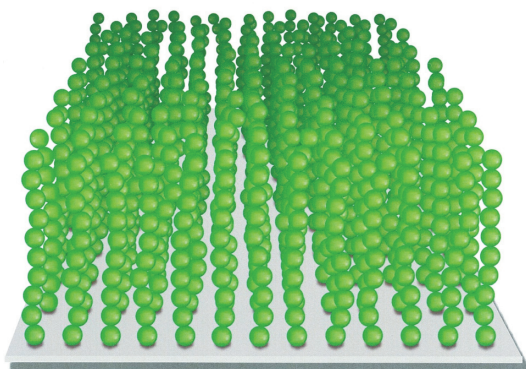


Figure 1. Schematic illustration of concentrated polymer brush.

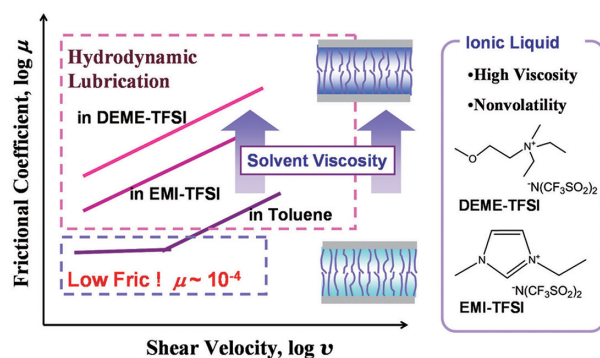


Figure 2. Schematic representation of the friction behavior of concentrated polymer brushes (CPBs) of poly(methyl methacrylate) in ionic liquids (DEME-TFSI and EMI-TFSI) and usual organic solvent (toluene).

Surface-Initiated RAFT Polymerization from Fine Particles

Monodisperse silica particles (SiPs) were surface-modified with a newly designed reversible addition-fragmentation chain transfer (RAFT) agent having a triethoxysilane moiety, 6-(triethoxysilyl)hexyl 2-(((methylthio)carbonothioyl)thio)-2-phenylacetate (EHT) (Figure 3). Surface-initiated RAFT polymerization of styrene was carried out with the EHT-modified SiPs in the presence of a free RAFT agent. The polymerization proceeded in a living manner, producing SiPs coated with well-defined polystyrene of a target molecular weight with a graft density as high as 0.3 chains/nm². Similarly, polymerizations of methyl methacrylate (MMA), *N*-isopropylacrylamide, and *n*-butyl acrylate were conducted, providing SiPs grafted with concentrated (high-density) polymer brushes. In all examined cases, the hybrid particles were highly dispersible in solvents for graft polymers, without causing any aggregations. Owing to exceptionally high uniformity and perfect dispersibility, these hybrid particles formed two- and three-dimensionally ordered arrays at the air-water interface and in suspension, respectively. In addition to the surface-grafting on SiPs, the versatility of this technique was demonstrated by carrying out surface-initiated RAFT polymerization of styrene from iron oxide nanoparticles modified with EHT.

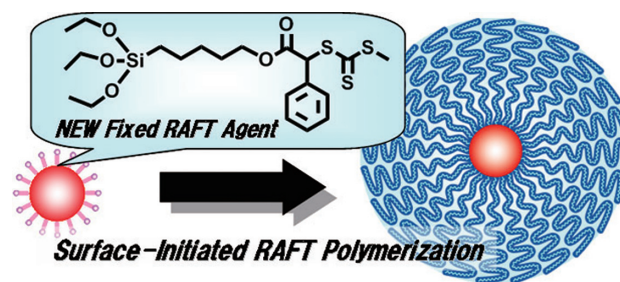


Figure 3. Chemical structure of a newly designed reversible addition-fragmentation chain transfer (RAFT) agent and schematic representation for surface-initiated RAFT polymerization to yield monodisperse silica particles (SiPs) grafted with concentrated (high-density) polymer brushes.