

Division of Materials Chemistry – Chemistry of Polymer Materials –

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Carnegie Mellon University, USA, 21 September
The University of Sydney, Australia, 24 June–21 July

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 Gels of Bottle Brushes Synthesized by Living Radical Polymerization

Successful application of living radical polymerization (LRP) made it possible to fabricate well-defined “concentrated” polymer brushes (CPBs), where graft chains in a good solvent were highly stretched, giving properties quite different and unpredictable from those of semi-dilute polymer brushes (SDPB). One of the most interesting properties of CPBs is the super lubrication in solvents, which was reasonably ascribed to CPBs never mixing with each other at any high compressions for the conformational entropic reason of highly extended chains. Such demixing or non-interpenetrating interaction can be expected also for comb-like polymers, so-called bottle brushes, depending on side-chain length; with increasing chain length, the effective graft density at the outermost surface should decrease through a crossover in brush regime from CPB to SDPB. In order to demonstrate this, we have synthesized well-defined bottle brushes of polystyrene (PS) with a high side-chain density by LRP with a multi-functional initiator and crosslinking them by coupling between radicals at side-chain ends as illustrated in Figure 1. Frictional measurement using an atomic force microscope revealed that the lubrication property was much improved on the gel surface by decreasing the side-chain molecular weight from 5600 to 1300 (see Figure 1), as expected. We believe that these studies will open up a new route to precision surface modification.

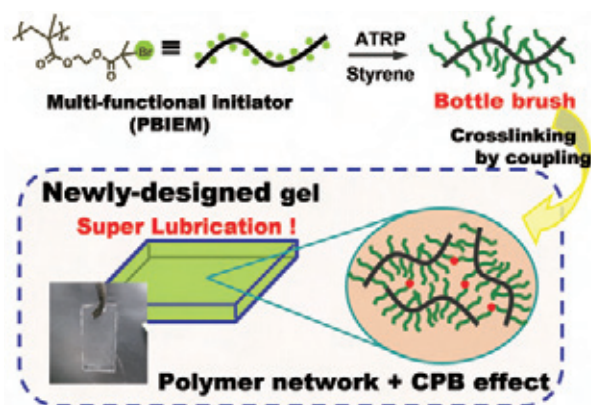


Figure 1. Synthesis of newly-designed gels of well-defined bottle brushes by LRP.

A Versatile Method of Initiator Fixation for Surface-Initiated Living Radical Polymerization on Polymeric Substrates

A facile yet robust approach to chemically fix an initiating group for atom transfer radical polymerization (ATRP) on various polymeric substrates was investigated. Conventional free radical copolymerization was conducted with methyl methacrylate (MMA), 2-(2-bromoisobutyryloxy) ethyl methacrylate (an ATRP initiator-carrying monomer, BIEM), and 2-((4-azidobenzoyl)oxy)ethyl methacrylate (a photoreactive phenylazide-carrying monomer, ABEM) in *N,N*-dimethylformamide at 75 °C, giving a random (statistical) copolymer (AIP). Thin films of the obtained copolymer were fabricated on poly(ethylene terephthalate) (PET) film surface by spin-casting a toluene solution of the terpolymer and were immobilized on the PET substrate via UV-irradiation using the photoreactivity of the phenylazido units. The surface-initiated ATRP (SI-ATRP) of poly(ethylene glycol) methacrylate (PEGMA) mediated by a copper complex was carried out in water at 30 °C in the presence of a sacrificial (free) initiator and the initiator-immobilized PET film as the solid substrate. The polymerization proceeded in a living fashion. The molecular weight of free polymer increased with polymerization time while retaining low-polydispersity index, and more importantly, the thickness of the poly(PEGMA) graft layer increased as a function of polymerization time with a reduced graft density (surface occupancy) as high as 0.5 in all examined time. This initiator immobilization technique was applied to various polymeric substrates including polystyrene, polypropylene, polyethylene, and polylactide. The fabrication of micropatterned polymer-brush surfaces was also demonstrated by photo-patterning the initiator layer followed by SI-ATRP.

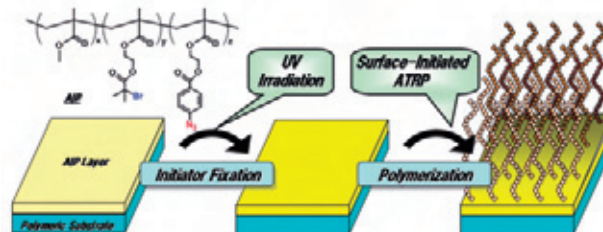


Figure 2. Chemical structure of phenyl azide- and atom transfer radical polymerization (ATRP) initiator-carrying random copolymer (AIP) and schematic representation for the immobilization of AIP on polymeric substrate followed by surface-initiated ATRP.