

# Division of Materials Chemistry

## – Chemistry of Polymer Materials –

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PIETRASIK, Joanna (Ph D)      Lodz University of Technology, Poland, 5 June–5 July

## 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  
Hybrid Materials                      Biointerface

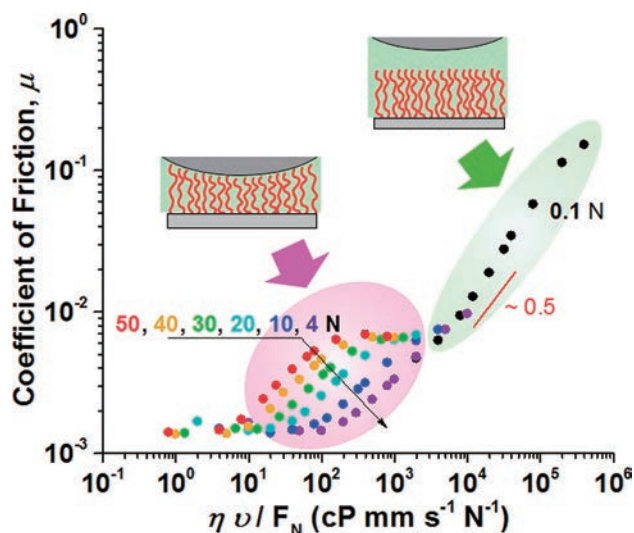


### Selected Publications

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**, 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).

## Soft and Resilient Tribology (SRT) Systems Using Concentrated Polymer Brushes

Concentrated polymer brushes (CPBs) have received much attention because of their super-lubrication property in good solvents, exhibiting ultra-low frictional coefficient ( $\mu$ ) on the order of  $10^{-4}$  revealed by AFM. We have revealed the lubrication mechanisms of CPBs, i.e., hydrodynamic and boundary lubrication, from the results of the swelling behavior as well as the solvent viscosity used for the microtribological measurements. Furthermore, the macroscopic super-lubrication property has recently been confirmed using extraordinarily thick CPBs synthesized under high-pressure surface-initiated atom transfer radical polymerization. Toward industrial applications, the issue of improving the durability/wearability/resiliency should be addressed. Here we demonstrate the tribological properties of thick poly(methyl methacrylate) (PMMA)-CPBs with an improved resilience in an ionic liquid, *N*-(2-methoxyethyl)-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (MEMP-TFSI). Figure 1 shows the Stribeck curves (friction profiles) of PMMA-CPBs using a macroscopic ball-on-disk setup at rt, where  $\eta$ ,  $v$ ,  $F_n$  represent viscosity of the solvent, sliding speed, and normal force, respectively. The low  $\mu$  as  $10^{-3}$  order under low sliding speeds was obtained in an extremely high normal force up to 50 N. Compared to the other soft-lubricating systems including the previously-reported CPBs, the resilient CPBs exhibited unique normal force-induced frictional increments over a wide range of sliding speeds. Such a deviation from the master Stribeck curve could be attributed to non-hydrodynamic effects owing to their viscoelastic properties of the swollen CPBs,

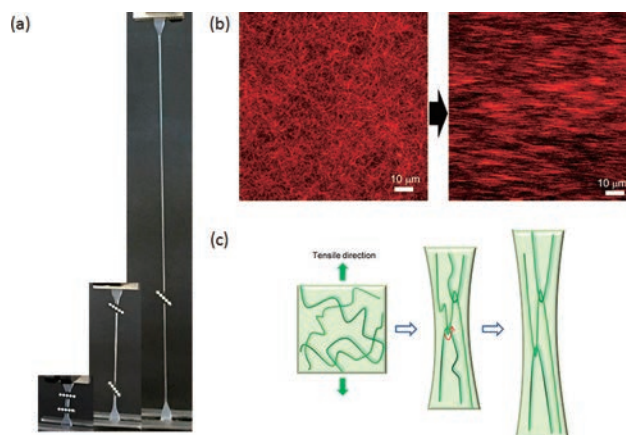


**Figure 1.** Plots of  $\mu$  vs  $\eta v/F_n$  for PMMA-CPB vs bare-glass measured in MEMP-TFSI at  $F_n = 0.1, 4, 10, 20, 30, 40,$  and  $50$  N.

which is a new mechanism to control the sliding surfaces upon high normal loads. The resilient CPBs have now been tested for various sliding surfaces including seals, bearings, and so on, with collaborations between chemical, rheological, informative, and machine engineering research groups.

## Strain Hardening of Highly Stretchable Elastomeric Composites Reinforced with Well-Defined Nanofiber Network of Bacterial Cellulose

Highly stretchable poly(ethyl acrylate) (PEA) composites reinforced with a well-defined nanofiber network of bacterial cellulose (BC) were prepared via stepwise solvent exchange followed by *in situ* photo-initiated free radical polymerization. Despite the small volume fraction of BC (approximately 0.4 vol%), the BC/PEA composite showed significant increases in Young's modulus (26 times larger than that of the neat PEA), tensile strength (3.5 times larger), and fracture energy (3.8 times larger), with its fracture strain (1520 %) almost the same as that of the neat PEA (1660 %). This composite was characterized by effective strain hardening. The changes in strain-hardening modulus and tensile strength were explained well by the rule of mixtures. Confocal laser scanning microscopic (CLSM) observations revealed the structure of the nanofibers embedded in the elastomeric matrix. The enhanced mechanical properties were based on the rigidity and flexibility of the BC nanofibers and their entangled network, and were ascribed to the well-defined BC nanofiber network produced by the bacterium.



**Figure 2.** (a) Images of the BC/PEA composite in the tensile tests; the strains were 0, 400, and 1400 % from left to right. (b) CLSM images of the composites before (left) and during (right) stretching, indicating high alignment of bacterial cellulose nanofibers. (c) Schematic illustration of the proposed BC-reinforcement mechanism of the BC/PEA elastomer.