Division of Materials Chemistry
- 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).

Research Activities (Year 2006)

Presentations

Fukuda T (invited), Surprising New Surface-Science of CPB: 28th Australasian Polymer Symposium, Rotorua, New Zealand, 5–9 February. Society of Rubber Industry Workshop, Uji, 21 April. BASF Asian Workshop on Nanostructured Surfaces, Shanghai, China, 5–11 May. Polymer Symposium, Osaka, 18 May. Tokai Polymer Symposium, Gifu, 25–26 August. 4th IUPAC International Symposium on Radical Polymerization, Lucca, Italy, 3–8 September. Society of Fiber Science and Technology Meeting, Kurashiki, 11 November. Kasenken Symposium, Kyoto, 15 November. Kansai Polymer Symposium, Osaka, 18 November. Riken Symposium, Wako, 28–30 November. Hokuriku Polymer Symposium, Fukui, 8 December.

Tsujii Y (invited), Precise Surface Modification by Surface-initiated LRP: New Technology Presentation Meeting, Tokyo, 27 September.

Ohno K (invited), Hybrid Particles with CPB: Macro Group UK International Conference on Polymer Synthesis, Coventry, UK, 31 July–3 August. Kyushu Polymer Symposium, Kagoshima, 24 November. KIPS Symposium, Kyoto, 1 December.

Goto A (invited), Kinetics of LRP: 55th Spring Meeting, Soc. Polym. Sci., Jpn., Nagoya, 24–26 May.

A New Family of Colloidal Crystals Formed by Suspensions of Silica Particles Grafted with a Concentrated Polymer Brush

A colloidal crystal was newly identified for a liquid suspension of the hybrid particles having a spherical silica core and a shell of well-defined poly (methyl methacrylate) (PMMA) concentrated brush. With increasing particle concentration, the suspension progressed from a (disordered) fluid to a fully crystallized system, going through a narrow crystal/fluid coexisting regime (Figure 1). The crystal had a face-centered-cubic structure with a surprisingly large nearest-neighbor interparticle distance, suggesting that the graft chains, highly extended due to the concentrated brush effect, exerted an interparticle steric potential of that long range. This type of colloidal crystal is new with respect to the origin of long-range interparticle potential and the controllability of many of the system parameters.

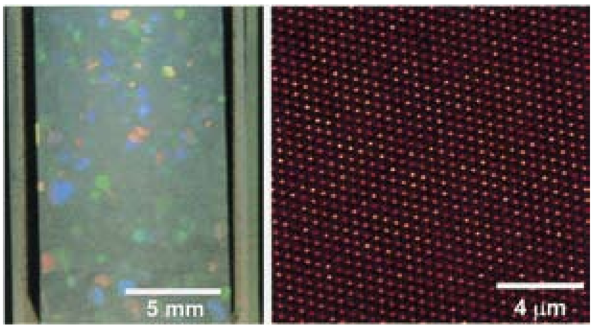

Figure 1. Photograph and confocal laser scanning microscopic image of colloidal crystal.

Ultra-low Frictional Coefficients between Solvent-Swollen Concentrated Polymer Brushes

The interaction forces between surfaces modified with PMMA brushes were measured in good solvent by atomic force microscopy. The semi-dilute brush (σ = 0.024 chains nm^{-2}, M_n = 90,000, M_w/M_n = 1.27) had two different regimes of friction (Figure 2): at low applied loads, the frictional coefficient μ was very low (< 0.001), and in the threshold region, it steeply increased with increasing applied load, approaching the limiting constant value of about 0.1. This transition was ascribed to the interpenetration of the brushes at high loads. Most interestingly, the μ value between concentrated brushes (σ = 0.53 chains nm^{-2}, M_n = 88,000, M_w/M_n = 1.17) showed no such transition, staying at low values, lower than 5×10^{-4}, in the whole range of loads studied. This μ value is one of the lowest of all materials and comparable to that achieved for polyelectrolyte semi-dilute brushes with the help of a charge effect. This extremely low frictional property was reasonably ascribed to the fact that swollen concentrated brushes would hardly interpenetrate each other due to the large osmotic pressure and highly stretched chain conformation (entropic interaction).

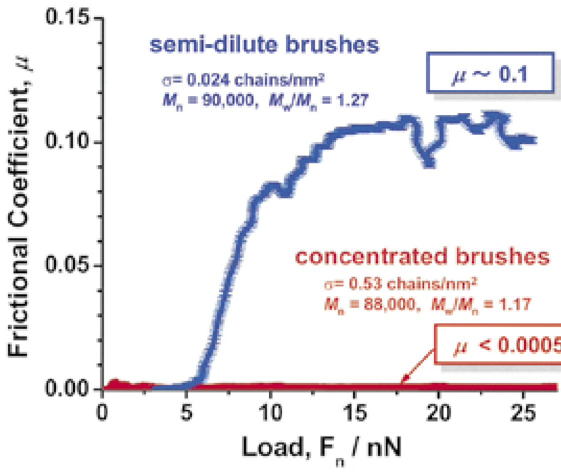

Figure 2. Plot of frictional coefficient μ vs. load for concentrated and semi-dilute PMMA brushes in toluene.

Grants

Fukuda T, Science and Technology of CPB, Grant-in-Aid for Specially Promoted Research, 1 April 2005–31 March 2009.

Tsujii Y, Creation of New Bio-Interfaces Based on CPB, Grant-in-Aid for Science Research (A), 1 April 2005–31 March 2008.

Tsujii Y, Patterning by Direct-Writing Graft Polymerization, Grant-in-Aid for Exploratory Research, 1 April 2005–31 March 2007.

Tsujii Y, Development of Ionic-Liquid Polymer-Based Electrolyte Membrane by Controlled Graft Polymerization, Strategic Development of PEFC Technologies for Practical Application Program by NEDO, 9 December 2005–20 March 2007.

Ohno K, Science of Semi-Soft Colloidal Crystals, Grant-in-Aid for Young Scientists (A), 1 April 2005–31 March 2008.

Ohno K, Fundamentals and Applications of Semi-Soft Colloidal Crystals, Industrial Technology Research Grant Program by NEDO, 1 January 2005–31 December 2007.