Division of Materials Chemistry
– Chemistry of Polymer Materials –

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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
Polymer Brush
Biointerface
Living Radical Polymerization
Hybrid Materials

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).

pMAIRS Analysis on Chain-End Functionalization of Densely Grafted, Concentrated Polymer Brushes

The degree of chain-end functionality in a densely grafted, concentrated polymer brush is a critical parameter. In this study, *p*-polarized multiple-angle incidence resolution spectrometry (pMAIRS) technique was applied to monitor the emergence and disappearance of substituted azide (N_3) at the chain ends of polymer brushes, allowing accurate determination of the azide density and the click reaction efficacy. The peak separation of the N_3 absorption bands in the pMAIRS spectra showed that azide substitution occurred not only at the brush ends but also at underlying initiators that did not react during surface-initiated atom transfer radical polymerization (Figure 1). Hence, the density of each type of azide group and the efficiencies of the azidation and click reaction could successfully be estimated. Furthermore, a chain-end-selective click reaction was demonstrated for the azide-functionalized polymethacrylate-type polymer brushes based on size exclusion effects and polarity differences. Thus, the pMAIRS method provides important quantitative information that can expand applications of chain-end-functionalized polymer brushes.

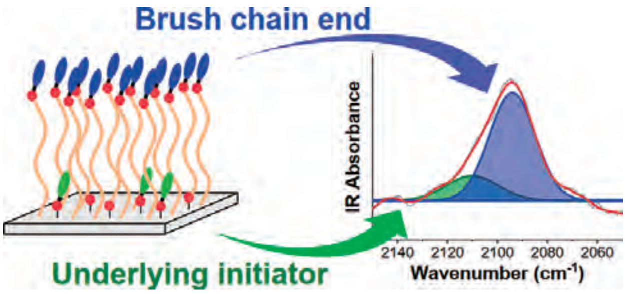

Figure 1. Peak separation of the N_3 absorption band in the pMAIRS spectra of an azide-functionalized polystyrene brush. Multiple Gaussian fitting highlights the peaks of brush-chain-end azides (blue) and azide-substituted initiators (green).

Main-Chain Stiffness of Cellulosic Bottlebrushes with Polystyrene Side Chains Introduced Regioselectively at the *O*-6 Position

We describe the conformational characteristics of a cellulosic bottlebrush, *i.e.*, a cellulose derivative of densely substituted side chains, in a dilute solution in order to clarify the effect of cellulosic main-chain stiffness and side-chain crowdedness. Novel cellulosic bottlebrushes **1** (Figure 2a) with polystyrene (PSt) side chains and methyl groups at the *O*-6 and *O*-2,3 positions, respectively, were highly regioselectively synthesized via a protecting group strategy in combination with a copper-catalyzed azide-alkyne coupling click reaction, yielding densely graft polymers where PSt chains were introduced in every anhydroglucose repeating unit, *i.e.*, at a "constant" distance of 0.5 nm along the cellulose backbone. Small-angle X-ray scattering (SAXS) measurements of **1** in dimethylformamide revealed that the cross-sectional radius of gyration depended on the degree of polymerization (*DP*) of the PSt side chains in accordance with the power law with an exponent of 0.50, indicating that the PSt side chains adopted extended conformation owing to the inter-side-chain interaction, *i.e.*, the excluded volume effect among the neighboring side chains. Size exclusion chromatography–multi-angle light scattering (SEC-MALS) experiments were conducted to determine the main-chain stiffness. Despite the use of a poor solvent for PSt, the stiffness parameter λ^{-1} was almost independent of the *DP* of the PSt side chains up to 60 even in the brush regime of side-chains with inter-chain interaction and hence somehow stretched conformation. This behavior differs from those of previously reported bottlebrushes of flexible main chains and successfully demonstrated the cellulosic main chain intrinsically so stiff to form bottlebrushes of sufficiently long side chains with little effect on the main-chain conformation (Figure 2b). This would expand the diversity in design of bottlebrushes along with the chirality of cellulosic chain.

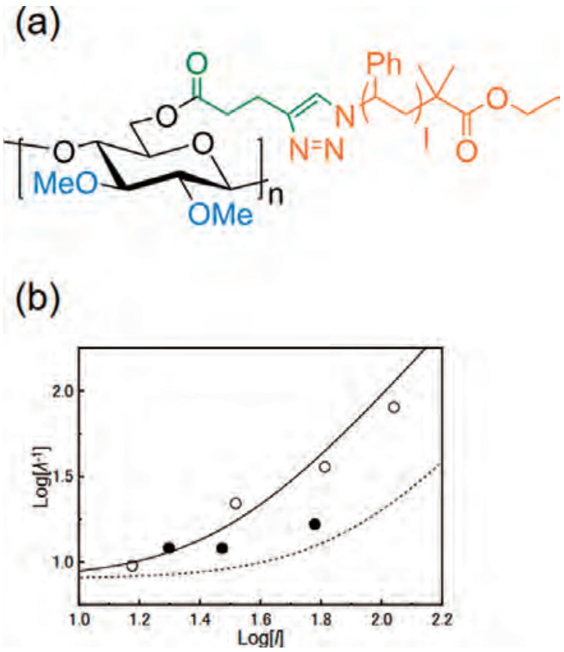

Figure 2. (a) Chemical structure of cellulosic bottlebrushes **1** with PSt side chains: *l* = 60, 30, and 20. (b) The dependence of λ^{-1} on the degree of polymerization (*l*) of the side chains for **1** in DMF/LiBr (filled circles) in this study and PSt-PSt bottlebrushes in cyclohexane (open circles) reported in literatures. The solid and broken lines represent theoretical curves for the PSt-PSt bottlebrush calculated with *h* = 0.27 nm (solid line) and *h* = 0.52 nm (broken line) in a Θ-solvent.