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
Living Radical Polymerization
Polymer Brush
Tribology
Hybrid Materials

Recent Selected Publications

Sakakibara, K.; Ishida, H.; Kinose, Y.; Tsujii, Y., Regioselective Synthesis of Cellulosic Janus Bottlebrushes with Polystyrene and Poly (ε-Caprolactone) Side Chains and Their Solid-State Microphase Separation, *Cellulose*, **28,** 6857-6868 (2021).

Kinose, Y.; Sakakibara, K.; Sato, O.; Tsujii, Y., Near-Zero Azimuthal Anchoring of Liquid Crystals Assisted by Viscoelastic Bottlebrush Polymers, *ACS Appl. Mater.*, **3,** 2618-2625 (2021).

Sakakibara, K.; Maeda, K.; Yoshikawa, C.; Tsujii, Y., Water Lubricating and Biocompatible Films of Bacterial Cellulose Nanofibers Surface-Modified with Densely Grafted, Concentrated Polymer Brushes, *ACS Appl. Nano Mater.*, **4,** 1503-1511 (2021).

Maguire, S. M.; Krook, N. M.; Kulshreshtha, A.; Bilchak, C. R.; Brosnan, R.; Pana, A.-M.; Rannou, P.; Maréchal, M.; Ohno, K.; Jayaraman, A.; Composto, R. J., Interfacial Compatibilization in Ternary Polymer Nanocomposites: Comparing Theory and Experiments, *Macromolecules.*, **54,** 797-811 (2021).

Maguire, S. M.; Boyle, M. J.; Bilchak, C. R.; Demaree, J. D.; Keller, A. W.; Krook, N. M.; Ohno, K.; Kagan, C. R.; Murray, C. B.; Rannou, P.; Composto, R. J., Grafted Nanoparticle Surface Wetting during Phase Separation in Polymer Nanocomposite Films, *ACS Appl. Mater. Interfaces.*, **13,** 37628-37637 (2021).

Synthesis of Cellulosic Janus Bottlebrushes with Polystyrene and Poly (ε-Caprolactone) Side Chains

Graft polymer with dense side chains is called bottlebrush. A type of bottlebrush (BB) possessing different types of side chains (Janus BB) attracts attentions as a building block for high-order structures because immiscible side chains could undergo microphase separation, where the main chain is located at the interface.

We have successfully synthesized a novel cellulosic Janus BB with polystyrene (PS) and poly(ε-caprolactone) (PCL) as side chains (Figure 1a). The two types of side chains were regioselectively grafted by "grafting-from" (for PCL at *O*-2,3 positions) and "grafting-to" (PS at *O*-6 position) techniques with the aid of a *p*-methoxytrityl protecting group. The degree of substitution (DS) of PCL (degree of polymerization (DP) = 100) was estimated to be 1.5, and that of PS was estimated to be 0.64–0.84 depending on its chain length (DP = 38, 90 or 158). As for the high-order structure of cellulosic Janus BB, annealed samples were observed by transmission electron microscopy (TEM) (Figure 1b). The cellulosic Janus BB (PS/PCL = 50:50 v/v) was revealed to form a lamellar microdomain structure with three layers. These layers were attributed to amorphous PCL, crystalline PCL, and amorphous PS layers, indicating that the main chain of the BB (cellulose) was located at the interface between amorphous PS and amorphous PCL layers and hindered the crystallization of PCL segments near the main chain. It is expected that further tuning of the structural parameters of cellulosic Janus BB could lead to chiral or helical high-order structures, bringing intriguing functionalities.

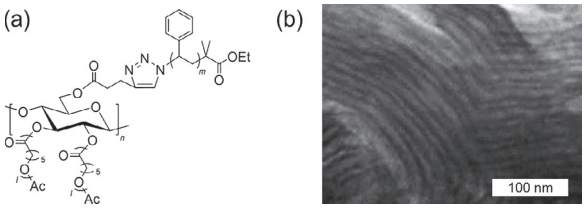

Figure 1. (a) Chemical structure of cellulosic BB and (b) TEM image of its annealed bulk film (PCL: DS = 1.5, DP = 100; PS: DS = 0.75, DP = 90).

Relaxation Behavior of Side Chain and Anchoring Property of Liquid Crystal on Cross-Linked Bottlebrush Polymer Film

The liquid crystals (LCs) in bulk can be aligned by external filed suchs as electric and magnetic fields, whereas the change in the direction of LCs near a surface is restricted by the interaction between LCs and the surface, which is known as the anchoring effect. In contrast to a strong anchoring case, it is difficult to fabricate an extremely weak anchoring (zero anchoring) surface with sufficient stability. It had been reported that the concentrated polymer brush and cross-linked BB (Figure 2a) comprised of poly(hexyl methacrylate) (PHMA) provided a zero-azimuthal anchoring property even at low temperature.

We have investigated the anchoring mechanism of LCs on a brush structure consisting of cross-linked films of PHMA BBs (Figure 2b). The azimuthal anchoring coefficient A_2 was estimated from the voltage–transmittance curves and found to decrease with increasing temperature in a certain temperature range (Figure 3a). Then, the rheological measurement for the mixture of BB and LC was carried out to discuss the relaxation behavior of the side chain of BB (Figure 3b). As a results, the characteristic temperature of the side-chain motion corresponded to the above-mentioned, A_2-decreasing temperature range (Figure 3a). This was also the case with the poly(ethyl methacrylate) (PEMA) BB system. Consequently, it was concluded that the weak anchoring of LCs on a polymer-brush-coated surface was attributed to the polymer-chain dynamics and that the A_2 value could be lowered by the brush structure achieving higher mobility as well as the brush chemistry promoting the swelling in LCs.

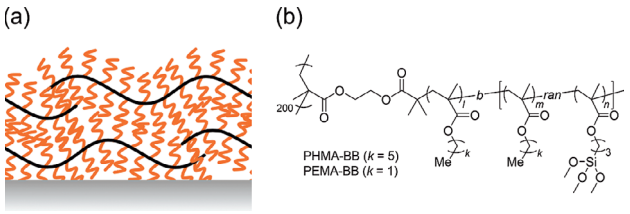

Figure 2. Schematic illustration of cross-linked BB film (a) and chemical structure of BB with cross-linking moiety (b).

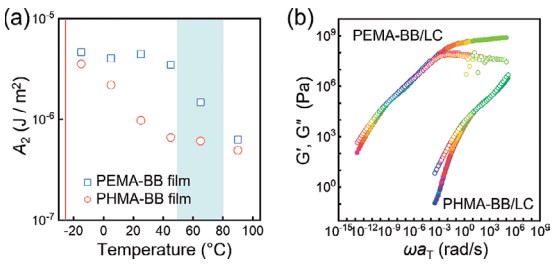

Figure 3. The relation between A_2 and temperature; the red line and blue shade indicate the characteristic temperatures of the relaxation of side chains for PHMA and PEMA BB films, respectively. (b) Master curves of G′ (filled circles) and G″ (open circles) for mixtures of PHMA-BB and PEMA-BB with LCs, respectively. Reprinted (adapted) with permission from Ref. No 1. Copyright 2021 American Chemical Society.