Hemicellulose-derived Xylan and Its Nanocrystal as Novel Polysaccharides to Tune Micro-phase Separated Block Copolymers for Advanced Applications

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Self-assembled block copolymers (BCPs) with micro-phase separated structures have attracted attention due to their potential applications as lithography material in the semiconductor industry and a soft template in the design of precisely ordered pore materials. The primary questions to be addressed include whether forestry bio-material xylan makes it possible to tune micro-phase separation window of BCP along with high Flory-Huggins's parameter BCP design. Additionally, xylan nanocrystals (XNCs) have potential to further tune micro-phase separation of BCP due to their unique rod- or platelet-like shape and high crystallization. The follow-up question to be addressed is how to design XNC-BCP hybrid nanocomposites with ordered nanostructure that work as a soft template to establish precisely organized pores in energy-material applications. The studies of xylan and XNC tailoring micro-phase separation of BCP open an avenue for its advanced applications.

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Tunable Micro-phase Separated Window of Block Copolymers *via* Hemicellulose-derived Xylan in Lithography Material Applications

Block copolymers (BCPs) are composed of chemically distinct chain segments *via* covalent bond linkages. Synthetic poly(styrene)-block-poly(methyl methacrylate) (PS-b-PMMA), as an example of a typical BCP, is primarily prepared synthetically *via* anionic or controlled free radical polymerization. PMMA and PS chain segments are not microscopically miscible, and they tend to thermodynamically self-assemble into different phase structures (*e.g.*, lamellar and cylinder structures) driven by micro-phase separation. Due to its unique micro-phase separated structures, the lamellar structure in 10 nm size of self-assembled PS-b-PMMA under either thermal or solvent-vapor annealing primarily works for lithography materials in the semiconductor industry (Tang *et al* 2008). As technology updates increase year-by-year, 10-nm size lithography materials in the semiconductor industry have gradually become out of date. As a consequence, the major countries of Japan, US, and South Korea are spending large amounts of money on lithography materials sized at 5 down to 1 nm (JSR Co., Japan, DuPont Co., USA, and Dongjin Semichem Co. South Korea, *etc*.). Unfortunately, self-assembled PS-b-PMMA in lamellar structure failed to reach the sizes down to 5 nm.

According to the phase diagram (Hiemenz and Lodge 2020), the micro-phase separated BCP is governed by the Flory-Huggins interaction parameter χ and degree of polymerization N. The χN product has to reach above a critical value (10.5 for symmetric

di-BCP & 17.9 for symmetric tri-BCP) in order to achieve micro-phase separation of BCP. Namely, increasing N or χ can enhance micro-phase separation of BCP and achieve its small size of lamellar structure. However, tuning molecular weight of chain segments has its intrinsic restrictions, as the glass transition temperature correlates with degree of polymerization. High annealing temperature is required for large molecular weight BCP during its self-assembly, and such conditions may lead to material decomposition. As an alternative approach, the development of BCP with high χ has attracted attention in both academia and in the semiconductor industry. One critical question is about how to tune the χ parameter and then push the size of BCP lamellar structure from 5 down to 1 nm for advanced lithography materials. The major countries of Japan, US, and South Korea in the semiconductor industry currently are racing to take the lead in advanced lithography technology (*e.g.*, Tokyo Ohka Kogyo Co., Japan, DuPont Co., USA, and Fujifilm Co., Japan), and the Netherlands and China are catching up with these countries regarding this technology. Inspired by the lamellar structure of linear saccharide-based BCP sized toward 10 to 5 nm, xylan as the hemicellulose derivative with linear and branched polysaccharide structure has potential for tailoring the Flory-Huggins χ parameter of BCP with a wide range of micro-phase separated lamellar structures. Such products are expected to work as probably 1 nm size lithography materials *via* tunable degree of polymerization and degree of substitution of side chains of xylan polysaccharide.

Unfortunately, academia has routinely regarded hemicellulose as trash after the separation of cellulose and lignin during the bio-refinery process, as hemicellulose itself has no prospects for use in material manufacturing either in solution casting films or melting process (Gu *et al* 2021). For the last few years, the hemicellulose-derived xylan has attracted increasing attention. Xylan is abundant in hardwood as the main polysaccharide of hemicellulose. Its merits primarily involve its relatively low molecular weight, easy dissolution in conventional polar solvents, and strong hydrophilicity. Most importantly, xylan with unique branch chains and abundant hydroxyl groups on both linear and branch chains have potential for tuning micro-phase separation window for designing xylan-based BCP with high χ parameter as lithography materials (Morita and Yamamoto 2017). Additionally, anionic and controlled free-radical and ring-opening polymerization are powerful tools to design xylan-based BCP with tunable phase structures and sizes. According to in-house and synchrotron X-ray wide and small angle scattering (SAXS and WAXS) in addition to grazing incident SAXS, different phase structures along with their sizes can be elucidated. For phase morphology analysis, electron microscopy (transmission electron microscope and atomic force microscopy) has unique merits and often works as a set of supplemental tools for scattering characterizations. Moreover, inspired by previous work regarding enhanced micro-phase separated poly(butyl acrylate-co-methyl methacrylate) copolymer (PMMA-co-PBA) driven by nanocellulose, CNC (Zhang *et al* 2019), we are curious as to whether xylan-derived nanocrystals have the same function to further tailor micro-phase separation of xylan-based BCP. We also want to know whether the resulting hybrid xylan nanocrystal (XNC)-BCP nanocomposite can self-assemble into ordered nanostructure for advanced pore material manufacturing.

Tunable Micro-phase Separated Structure of BCP Nanocomposites *via* Xylan Nanocrystal as a Soft Template for Constructing Organized Pore Materials

Xylan has been considered as an amorphous material for the past several years, while the crystalline structure of xylan has been produced *via* its deacetylation or de-branching, assisted with solvents, such as dimethyl sulfoxide and water (Meng *et al* 2021). The typical morphology of xylan nanocrystal is plate- or rod-like morphology. Inspired by rod-like CNC for tuning micro-phase separation of polyurethane and PMMA-co-PBA, XNC has large potential to further tailor micro-phase separation of BCP. However, current research on XNC is almost a blank in the polymer field regarding polymer nanocomposites and BCP, which is possibly due to its short history since its discovery. However, recent study in terms of polysaccharide-based BCP enhances the feasibility of tunable micro-phase separation of BCP driven by XNC (Chen *et al* 2024). Additionally, as another tough question, the miscibility between hydrophilic XNC and BCP is a challenge in achieving enhanced micro-phase separation. Ligand-decorated XNC (L-XNC) sounds like a feasible approach to mediate the miscibility and phase separation of hybrid L-XNC and BCP nanocomposites, which can be attributed to the ligand guiding hydrogen bond interactions (Warren *et al*. 2008). The phase structures and morphology of L-XNC and BCP nanocomposites are usually confirmed *via in-situ* SAXS and WAXS and electron microscopy. Small-angle neutron scattering as a supplement tool contributes to its inter-phase structure elucidation. These XNC and BCP hybrid nanocomposite materials with organized nanostructure as a soft template make it possible to produce ordered pore materials for energy-material applications.

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