【Grant-in-Aid for Scientific Research (S)】

A Study of Sequence-Controlled Polymers: Sequence Properties and Game-Changing Materials

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Purpose and Background of the Research

●Outline of the Research

Proteins can be regarded as sequence-controlled “copolymers” of amino acids, and sequence is the most essential primary structural factor that determines their properties. The cooperation of various repeating units in well-defined sequence are the uniqueness of the natural polymers, as opposed to synthetic polymers. Studies in sequence-dependent properties/functions through syntheses of sequence-controlled synthetic polymers will lead to the progress of polymer science as well as the development of advanced and smart polymeric materials. The development of precision polymerizations has allowed us to synthesize polymers having controlled molecular weight (length) and tacticity (direction of side chains), end-functionalized polymers, block copolymers, and graft copolymers, and the relationship between structure and physical properties have been clarified. On the other hand, some attempts to control sequence have been made all over the world in these several years, but few studies have clarified sequence-specific properties and functions. In this research project, we will achieve a library synthesis of alternating copolymers made of commodity monomer units carrying various pendant groups toward elucidation of sequence-dependent properties/functions through comparison with the corresponding statistical copolymers, leading to the development of innovative materials where sequence is crucial.

●Purpose of the Research

Alternating copolymers made of commodity monomer units such as (meth)acrylate, styrene, and acrylamide with various pendant groups are precisely synthesized (Figure 1). The corresponding statistical copolymers (sequence-uncontrolled polymers) are also synthesized for comparison of physical properties.

We will clarify the characters specific to alternating copolymer beyond conventional polymer science regarding glass transition temperature, crystallinity, self-assembly, stimulus responsiveness, mechanical properties, and interface properties. Furthermore, we will develop game-changing materials based on controlled sequence.

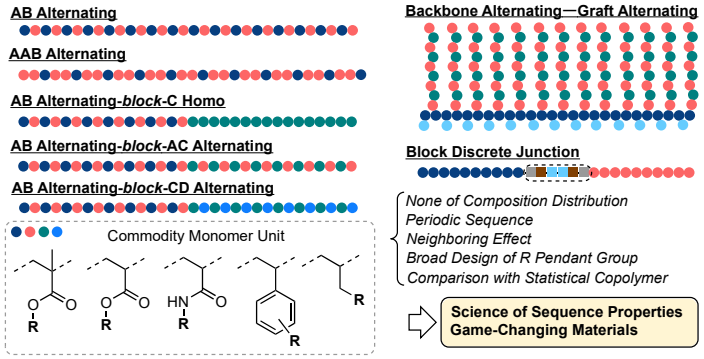

Figure 1. Polymer science of sequence properties with various types of sequence-controlled polymers and development of game-changing materials based on controlled sequence.

●Library Synthesis of Alternating Copolymers with Pendant-Transformable Monomer

Alternating copolymers made of commodity monomer units are synthesized from pendant-transformable monomers (Figure 2). The pendant transformation strategy allows a library synthesis of alternating copolymers with various pendant groups, which is helpful for exploring sequence-oriented properties. These monomers are rationally designed for control of selective cyclopolymerization or alternating copolymerization as well as subsequent transformation into commodity monomer units.

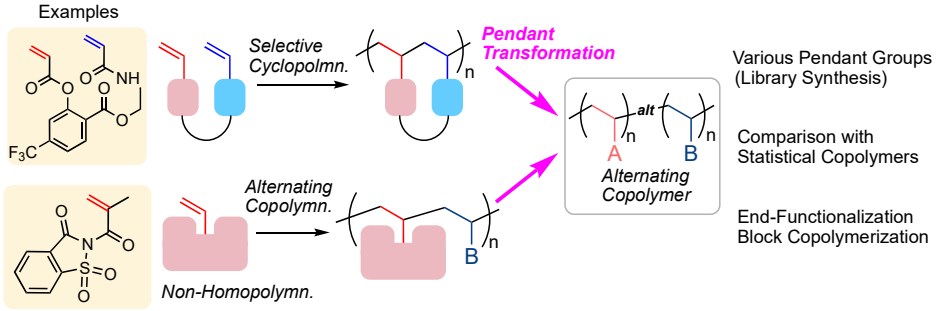

Figure 2. Library synthesis of alternating copolymers via polymerization and subsequent pendant transformation

Expected Research Achievements

●Effects of Sequence on Physical Properties

It is important to understand the hierarchical thermal chain mobility for control of the properties and functions of polymeric materials. In particular, the glass transition based on the relaxation of polymer backbone is a crucial behavior that can change the macroscopic physical properties, such as elastic modulus and viscosity coefficient. We will evaluate the segment dynamics of the alternating copolymers to clarify the effect of sequence on the glass transition behaviors beyond conventional theory such as Fox equation for prediction of T_g for copolymers from averaged composition ratio. Effects of sequence on self-assembly and interface properties are also studied.

●Development of resist materials for advanced semiconductors

Control of perpendicular orientation and long-range alignment of microphase-separated domains with block copolymer is fundamental to the fabrication of ultra-precise circuit patterns for next-generation semiconductor resist materials. Random copolymers have been used for neutralizing the substrate interfacial energy (Figure 3), however, aperiodic formation of the domain structure and structural defects in the domains are unavoidable, which is the big issue of this technique. In this research, we use alternating copolymers and/or alternating graft copolymers to neutralize the substrate or block copolymers whose junction is modified with sequence-defined oligomers to achieve the defect-free patterning.

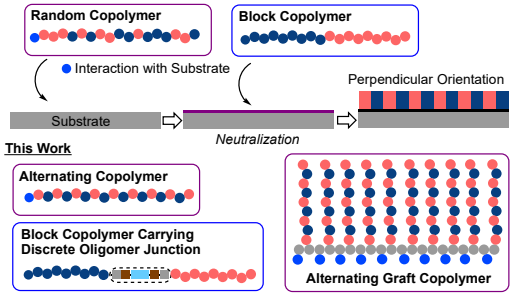

Figure 3. Advanced resist materials

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