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Studies on Characterization of Novel Acrylamide-Type Stimuli-Responsive Polymers and Their Coacervates for Intelligent Materials

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1. Introduction

In recent years, intelligent materials based on stimuli-responsive polymers have received significant attention because they can change their physico-chemical properties in response to small environmental changes. Among the stimuli-responsive polymers, poly(*N*-isopropylacrylamide) (PNIPAAm) is one of the most studied and used polymers in many fields. PNIPAAm shows a drastic soluble-insoluble change in aqueous media above its lower critical solution temperature (LCST). In order to develop PNIPAAm by introducing a reactive functional group, our research group has previously designed a novel carboxylated NIPAAm-based monomer, 2-carboxyisopropylacryl-amide (CIPAAm). The resultant NIPAAm-CIPAAm copolymer could show a very sensitive thermo-responsive behavior, indicating that we can successfully introduce a reactive functional group onto PNIPAAm without losing its intrinsic sensitive thermoresponse.

In this study, the author newly designed a hydroxylated NIPAAm-based monomer, 2-hydroxyiso-propylacrylamide (HIPAAm), and characterized poly(NIPAAm-*co*-HIPAAm). Moreover, it was found that both poly(NIPAAm-*co*-HIPAAm) and poly-(NIPAAm-*co*-CIPAAm) can show stimuli-responsive coacervates as described later, the author therefore analyzed and developed the stimuli-responsive coacervates of these copolymers.

2. Results and Discussions

Based on the estimated monomer reactivity ratios, the resultant poly(NIPAAm-*co*-HIPAAm) has a random comonomer sequence and a homogenous distribution of comonomer composition. Poly(NIPAAm-*co*-HIPAAm) could show a very sensitive thermoresponse in aqueous media despite including many hydrophilic groups, due to their random comonomer sequence and the continuous structure of the isopropylamide groups on the side chains. Moreover, the author demonstrated that the copolymers with a low HIPAAm content undergo a liquid-solid phase transition involving a coil-globule transition above their LCSTs, while the copolymers with a high content show a liquid-liquid phase separation accompanied by coacervation. The particle size of the coacervate droplets as well as the LCST could be easily controlled by the HIPAAm composition. The author clarified that the number of water molecules dissociated from the polymer chains above the LCST has a significant influence on whether the copolymer shows the coil-globule transition or the coacervation as well as the formation behavior of the coacervate. As for poly(NIPAAm-*co*-CIPAAm), it can show both the coil-globule transition and the coacervation in response to a pH change. So, by utilizing the coacervate induced in the binary poly(NIPAAm-*co*-HIPAAm) and poly-(NIPAAm-*co*-CIPAAm) aqueous system, the author could successfully prepare the fine stimuli-responsive semi-IPN microgel although it can be prepared in a simple and easy method without any additives.

3. Conclusions

In this thesis, the author demonstrated that the well-defined molecular design of the PNIPAAm-based polymers considering the molecular structure of the NIPAAm significantly contributes to their superior stimuli-responsive behavior, such as their sensitivities and the formation of the fine coacervate. The author believes that such a molecular design should be a significant concept and that these PNIPAAm-based functional polymers can serve as an “intelligent material” in various fields.

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