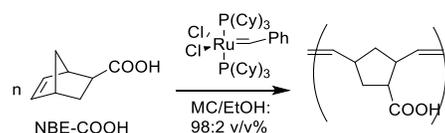


1. PRF#: 57743-UR7
2. Project Title: Regulating Self-Assembly of Short-Chain Amphiphilic Polymers
3. P.I. Name, Affiliation: Jun-Hyun Kim, Department of Chemistry, The Board of Trustees of Illinois State University
4. Co-PI (if any), Affiliation: N/A

Research progress

The PI group has focused on the examination of the structural changes of short-chain amphiphilic poly(norbornene) alcohol derivatives obtained by ring-opening metathesis polymerization (ROMP). The synthesis of norbornene-based monomers equipped with six different short-chain alcohol groups (C:OH ratios range from 3.5:1 to 7:1) and their polymerization were successfully completed (Figure 1). In addition, the assembly of the resulting linear polymers was performed in various solvents. Particularly, alcohol solvents readily allowed for controlled assembly into spherical nano/micro-scale particles. We found that the size of these homopolymer particles were precisely controlled by the molecular weights (MWs) (i.e., chain length) and the concentration of the linear polymers. In addition, the ratio of C:OH in the NBE backbone was found to be an important parameter for the assembly of linear polymers into well-defined structures. These findings have been summarized as a manuscript, which will be submitted shortly.

Furthermore, norbornene carboxylic acid (NBE-COOH) was polymerized via ROMP to evaluate the degree of polymerization and their assembly process. Based on the MW analysis by gel permeation chromatography (Figure 1), the targeted MWs were far from the experimental MWs for poly(NBE-COOH). This inefficient polymerization of the NBE-COOH monomer by ROMP could be due to the deactivation of Grubbs catalyst by the COOH functional groups. The use of high concentration of



| Targeted MW | 2760 (20 mers) | 5520 (40 mers) | 11040 (80 mers) | 16500 (120 mers) |
|------------------|-------------------|-------------------|--------------------|---------------------|
| Experimental MW | 799 | 2606 | 4509 | 2413 |
| Experimental PDI | 1.13 | 1.31 | 1.48 | 1.55 |

Figure 1. Poly(NBE-COOH) via ROMP and the degree of polymerization

monomers (120 mers) notably decreased the polymerization efficiency of NBE-COOH. To improve the polymerization efficiency, ROMP of NBE-carboxaldehyde (NBE-CHO) was carried out to yield the linear polymer with the targeted MW (Figure 2). The subsequent oxidation step allowed for the conversion of poly(NBE-CHO) to poly(NBE-COOH). Our current efforts involve the preparation of poly(NBE-COOH) precursors (e.g., NBE-carbonitrile, NBE-dicarboxylic anhydride) to perform ROMP, followed by the oxidation of the resulting linear polymers to prepare poly(NBE-COOH) derivatives whose MWs are comparable to poly(NBE) alcohols. The assembly of these linear homopolymers will then allow us to understand the structural changes based on the ratio of C:COOH.

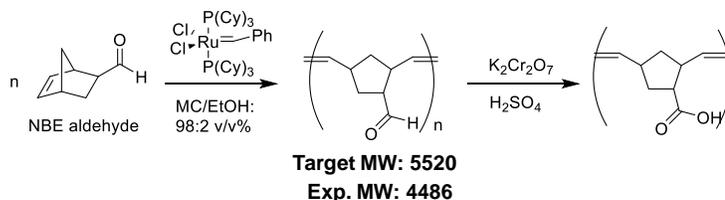


Figure 2. ROMP of (NBE-carboxaldehyde) and their subsequent oxidation to form poly(NBE-COOH).

In the meantime, the PI group also studied temperature-responsive poly(N-isopropylacrylamide), which can undergo structural changes (i.e., swelling and deswelling) as a function of temperature. This type of polymer often exhibits consolvency in a mixture of water and alcohol solvents. However, the PI group found a way to eliminate these properties. Regulating the structural properties of these polymers could provide us better insight into the molecular level interactions associated with various solvents. If a fully swollen

structure of polymer particles can be maintained, a wide range of guest molecules and/or nanoscale materials can be integrated into the polymer template, allowing us to examine the main driving force behind their interactions. As a proof of principle, we employed these polymer particles as a host template to incorporate gold nanoparticles as guest materials (Figure 3). Upon the preparation of the composite particles, examining the color of solution and/or absorption patterns of the guest gold nanoparticles demonstrates the cononsolvency and temperature responsiveness of the polymer particles in various solvents.

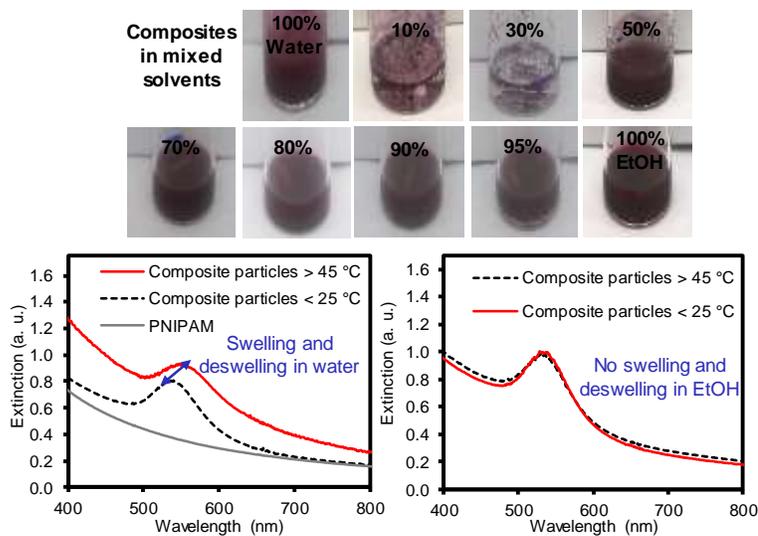


Figure 3. Cononsolvency and temperature-responsiveness of poly(NIPAM) particles loaded with gold nanoparticles.

Studying the physical behavior of these composite particles and their potential applications in chemical reactions resulted in successful publications (ChemPhysChem and Nanotechnology).

Impact on the PI and his students for career development

In this funding period, the PI tried to recruit more students (even accepting students who could only work a few weeks in the summer) to increase and broaden the participation of a wide range of students. These students were heavily involved in the synthesis of monomers and transformation of polymer functional groups. Their progress and new findings were shared through regular group meetings to understand the entire research project. By having more students even for a short period time, the PI had a great opportunity to hear many different ideas and challenges from students of various grade levels. Some of the results were presented at the ACS local section at Illinois Wesleyan University (Fall 2018) and the ACS national meeting in Florida (Spring 2019). The students gained valuable experiences in terms of broadening their research community and expanding their academic visions as well as searching for academic and industrial R&D positions. In addition, the work described in this progress report was published in ChemPhysChem and Nanotechnology journals. These outcomes enabled the PI to put together applications in 2019 for his promotion and his students to obtain enough data for their MS theses. Not only did students gain valuable experiences, five undergraduate students learned synthetic/polymerization skills and must-know instrumentations (GC, HPLC, UV, IR, XRD, SEM, etc) to be prepared for the new semester and student teaching as well as job searching.