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2. Project Title: Regulating Self-Assembly of Short-Chain Amphiphilic Polymers
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Introduction

The assembly of functional polymers into nanoscale morphologies has played an important role in many emerging technological applications including microreactors, environmental toxin sequesters, and drug-delivery vehicles. In such assembly processes, properly designed amphiphilic diblock- and triblock-copolymers have often shown controlled structural changes into micelles, vesicles, rods, tubes, disks, cylinders, and spherical particles. These assemblies are generally driven by the mutual immiscibility of the polymer blocks and the immiscibility of one of the blocks in a solvent or solvent mixture. Thus, both the size and morphology of the assemblies (either in solution, in bulk, or at the interfaces) are controlled by the molecular weight (MW) of polymers, the relative block length of the hydrophobic-to-hydrophilic groups, and the chemical/physical nature of repeating monomeric units. Here, we investigated the assembly process of highly simplified linear homopolymers with regularly-spaced, short-chain hydrophilic and hydrophobic groups (e.g., the tunable amphiphilicity of polymers at the repeating unit level) into well-defined shapes to fully understand their structural behaviors with minimal variables. Specifically, a series of norbornene (NBE)-based monomers armed with short-chain hydrophilic alcohol groups was prepared via ring-opening metathesis polymerization (ROMP), and their structural and morphological changes were thoroughly examined to form well-defined and size-tunable spheres in alcohol solvents as a function of concentration, ratio of C:OH, and MWs.

Results

As planned, we have extensively synthesized and characterized various NBE alcohol derivatives equipped with different ratios of C and OH groups [e.g., NBE-OH, NBE-(OH)₂, NBE-MeOH, NBE-(MeOH)₂]. Overall yields of these reactions were found to be typically less than 20% except NBE-MeOH (80%) and their purities of isolated monomers (by GC and NMR) were high enough to perform ROMP to form linear short-chain amphiphilic homopolymers of poly(NBE-alcohol) derivatives.

During ROMP of these monomers, the resulting polymers have shown a high tendency to precipitate out in a CH₂Cl₂ solvent. Under various optimization processes, a mixture of CH₂Cl₂ and THF (or EtOH) solvents allowed for the reliable formation of amphiphilic homopolymers. The linear polymers as prepared exhibited ill-defined structures and only showed a good solubility in relatively hydrophilic organic solvents (e.g., MeOH, EtOH, acetone, THF). Throughout the solvent screening process, alcohol solvents allowed all poly(NBE) alcohol derivatives to assemble into well-defined structures (Figure 1). Unlike other long-chain homopolymers or copolymers, varying the MWs and amount of polymers in solvent systematically affected the formation of well-defined sphere particles ranging from nanometer to micrometer size. This interesting behavior could be presumably caused by the restructuring process of the linear short-chain amphiphilic poly(NBE-OH) into spherical particles to locally minimize the surface energy/tension.

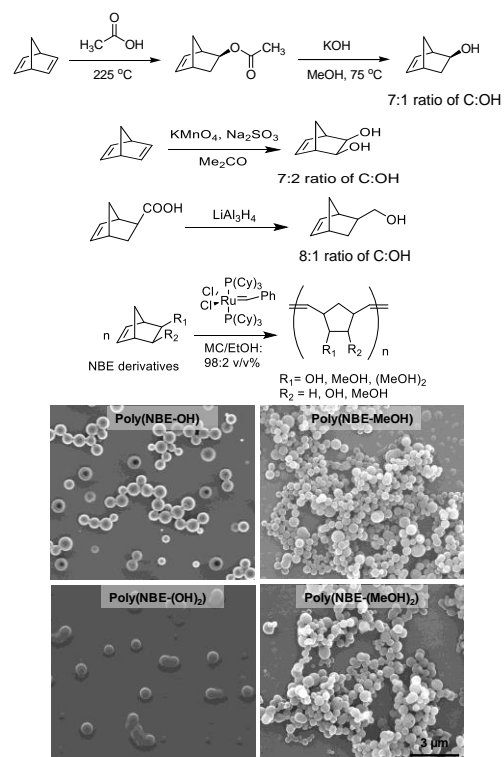


Figure 1. Examples of synthesized NBE-alcohol derivatives and corresponding SEM images of ROMP polymers.

To understand the minimum amount of polymer needed to form spherical particles by assembly (e.g., possibly comparable to the conventional critical micelle concentration, CMC), turbidity and DLS measurements were performed as a function of polymer concentration. Generally, turbidity and scattered light counts per second gradually increased with the increase of polymer amount, but did not show a distinctive Sigmoidal curve pattern to determine a sharp slope change corresponding to the CMC concentration. While typical non-ionic amphiphilic polymers exhibit CMC at 10^{-3} - 10^{-4} M, our linear homopolymers appeared to assemble into well-defined spherical structures at all concentration ranges we tested (i.e., concentration independent aggregation behaviors between 0.003 wt% and 0.1 wt%). With an increase of polymer concentration, the DLS measurements showed the systematic increase of hydrodynamic diameter of polymer particles which were measured to be much larger than those estimated by SEM due to the presence of strong hydrogen bonding. These measurements clearly confirmed that the amount of polymer concentration and MWs directly affected overall diameter changes of polymer particles.

The assembly of these short-chain amphiphilic homopolymers into uniform particles in alcohol solvents found to be very different from the conventional block copolymer and long-chain homopolymer systems, which could undergo a distinctive control of solvent interactions with repeating units of the polymers. In addition, it has reported that linear polymers possessing dualistic character of each repeating monomeric unit typically have a tendency to form thermodynamically stable anisometric globular structures. However, our short-chain linear poly(NBE-OH) assembled into only spherical shapes in alcohol solvents and did not form any well-defined structures in other solvents. Thus, we are currently investigating how these poly(NBE) equipped with a short-chain hydrophilic group undergo assembly into spherical particles in alcohol solvents. To the best of our knowledge, this is the first instance that spherical particles consisting of a wide range of sizes (from the nm- to μm -scale) are systematically controlled by the MW and concentration of short-chain homopolymers. Understanding the systematic formation of uniform spherical polymer particles from these types of short-chain amphiphilic polymers in various solvent media can allow for the development of a highly simple strategy that can be applicable to mass transformation of diverse amphiphilic polymers into well-defined structures.

Impact

Our extensive work with poly(norbornene) alcohol derivatives demonstrates how short-chain amphiphilic polymers assemble into well-defined structures by controlling the ratio of hydrophobic C and hydrophilic OH groups. The short-chain amphiphilicity highly affects interfacial forces between polymer chains and solvents, possibly causing the hydrogen-bonding induced assembly process to form thermodynamically stable structures.

Impact on the PI and his students for career development

As our department currently does not offer polymer-related courses, students who are involved in this project were able to experience a bit of polymer and materials chemistry through this research opportunity. The project was split into two parts where graduate students mainly focused on the characterization/understanding of the assembly process of homopolymers in solution, and undergraduate students were heavily involved in the synthesis of monomers and polymers. However, sharing results through regular group meetings, both the graduate and undergraduate students were able to fully understand how the entire project associated with polymer and materials chemistry progressed. I believe that this small group enrichment setting allowed each student to act as their group's representative many times, facilitating the improvement of communication skills that allowed for the assessment of the students' progress throughout the research period. In addition, the students could broaden their experiences in new fields of chemistry that haven't been learned in class before moving to real world science. The PI has a great opportunity to heavily focus on understanding the assembly of polymers in atomic repeating units and disseminate/expand his expertise to/with (under)graduate students through research and discussion on a daily basis.

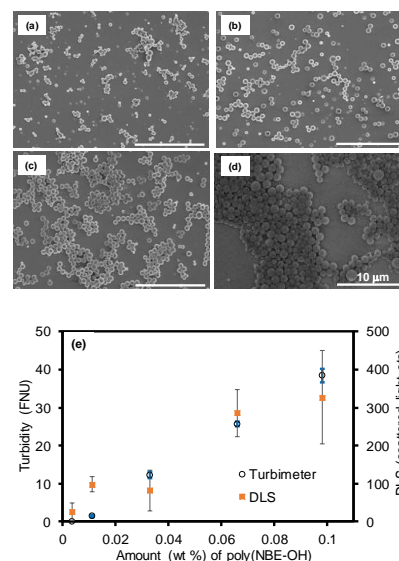


Figure 2. Representative SEM images of 40-mer poly(NBE-OH) in MeOH as a function of concentration: a) 0.01 wt%, b) 0.025 wt%, c) 0.05 wt%, and d) 0.1 wt% as well as d) their corresponding turbidity/DLS measurements.