APPLICATION OF CONTROLLED RADICAL POLYMERIZATION IN THE DEVELOPMENT OF
POLYMERS WITH BRANCHED ARCHITECTURES

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APPLICATION OF CONTROLLED RADICAL POLYMERIZATION IN THE DEVELOPMENT OF POLYMERS WITH BRANCHED ARCHITECTURES

Abstract

by

Xiaofeng Wang

Various synthetic methodologies for preparation of functional polymers with branched architectures by using atom transfer radical polymerization (ATRP) of AB* inimers (containing initiator fragment B* and monomer vinyl group A in one molecule) and reversible addition-fragmentation chain transfer (RAFT) polymerization of polymerizable chain transfer agents (transmers) are discussed. The target of this body research is mainly focused on development of new methodologies for synthesis of hyperbranched polymers and hyperbranched-star (hyperstar) polymers with controlled structures and site-specific functionalities via controlled radical polymerization (CRP) techniques. The main tools used to achieve this goal include controlled radical self-condensing vinyl polymerization (SCVP) and chain extension polymerization in solution and heterogeneous microemulsion and seeded emulsion. Research progress on the use of radical polymerization to introduce branching points into polymers via CRP methods is discussed in the introductory chapter. Chapter 2 describes the application of microemulsion and seeded emulsion to produce core-shell structured hyperstar
polymers in a one-pot process with activators generated by electron transfer (AGET) ATRP technique without worrying about the hyperstar-hyperstar coupling reactions.

Chapter 3 presents the synthesis of high-molecular-weight hyperbranched polymers ($M_n \sim 10^6$) via RAFT polymerization through copper-catalyzed trithiocarbonate transmer.

Chapter 4 discusses a facile approach for successful synthesis of hyperbranched polymers with high molecular weight and uniform structure by a one-pot polymerization of transmers initiated using copper catalyst in a microemulsion.
To all I love
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The properties and functions of polymeric materials are not only dictated by their compositions but also their structural arrangements (i.e. architecture). Exploration of polymers with novel molecular architectures has become a practical strategy for developing advanced soft nanomaterials essential to emerging nanotechnologies. Utilizing a combination of modern synthetic chemistries including atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer (RAFT) polymerization, microemulsion polymerization, this body of research resulted in the development of facile, versatile and highly efficient synthetic pathways for the preparation of structurally controlled macromolecular architectures of branched polymers and hyperbranched star (hyperstar) polymers.

Chapter 2 reports the application of microemulsions and seeded emulsions to produce core-shell structured hyperstar polymers in a one-pot process without worrying about hyperstar-hyperstar coupling reactions. The synthesis started with the ATRP self-condensing vinyl polymerization (SCVP) of an AB* inimers (containing initiator fragment B* and monomer vinyl group A in one molecule) in a microemulsion to produce hyperbranched polymers with high molecular weight, low dispersity, and a high density of bromine initiating groups. After the complete conversion of the inimer, a second
batch of monovinyl monomers was added \textit{in-situ} without destabilizing the microemulsion to subsequently grow radiating arms from these hyperbranched polymer macroinitiators (MIs) to produce well-defined hyperstar polymers.

To expand the application of microemulsion with controlled radical polymerizations (CRP) to provide better control over branched polymers, Chapter 3 presents the synthesis of high-molecular-weight hyperbranched polymers ($M_n \approx 10^6$) via polymerization of polymerizable chain-transfer agents (i.e., transmers) through copper catalyst initiation. Traditional RAFT homopolymerization of transmers that used thermal initiator, such as 2,2'-azo-isobutylnitrile (AIBN), as radical source only produced hyperbranched polymers with low molecular weights ($M_n < 10^4$) due to 1) the incorporation of initiator fragment at the focal point of hyperbranched polymers, and 2) the absence of radicals after certain time. In contrast, the new initiation system using a copper catalyst to activate the alkyl trithiocarbonate (i.e., a pseudohalogen) ensured a vinyl group at the focal point of every hyperbranched polymer and longer time of radical availability, resulting in the production of hyperbranched polymers with over-a-million molecular weight.

Chapter 4 discusses a facile approach for successful synthesis of hyperbranched polymers with high molecular weight and uniform structure by a one-pot polymerization of transmers with initiation of copper catalyst in a microemulsion. The segregated space in the microemulsion confined the inimer polymerization and particularly the polymer-polymer reaction within discrete nanoparticles. At the end of polymerization, each nanoparticle contained one hyperbranched polymer that had thousands of inimer units.
and low dispersity. The hyperbranched polymers were used as multifunctional macroinitiators for synthesis of hyperbranched star (hyperstar) polymers.

This Thesis also includes two Appendixes discussing parts of my Ph.D. research focusing on three other projects. The first project investigates the application of hybrid magnetic nanoparticles (MNPs) with well-defined core-shell structure, pH-tunable interfacial activity and strong magnetic responsiveness as recyclable stabilizers for oil-water separation (Appendix A). The second project discusses a metal-free ATRP system to produce hyperbranched polymers with photo catalyst. The preliminary results show that hyperbranched polymers could be produced in solution. When conducting the polymerization in a microemulsion system, a much higher molecular weight and low dispersity could be achieved.
ACKNOWLEDGMENTS

This thesis is dedicated to my parents, my wife and my son for their unconditional love, support, and confidence in me through these years.

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<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>ATRP</td>
<td>Atom transfer radical polymerization</td>
</tr>
<tr>
<td>RAFT</td>
<td>Reversible addition-fragmentation chain transfer</td>
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<tr>
<td>SCVP</td>
<td>Self-condensing vinyl polymerization</td>
</tr>
<tr>
<td>CRP</td>
<td>Controlled radical polymerization</td>
</tr>
<tr>
<td>AGET</td>
<td>Activators generated by electron transfer</td>
</tr>
<tr>
<td>CR-SCVP</td>
<td>Controlled radical self-condensing vinyl polymerization</td>
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<tr>
<td>NMR-SCVP</td>
<td>Nitroxide-mediated radical self-condensing vinyl polymerization</td>
</tr>
<tr>
<td>ATR-SCVP</td>
<td>Atom transfer radical self-condensing vinyl polymerization</td>
</tr>
<tr>
<td>ATR-SCVCP</td>
<td>Atom transfer radical self-condensing vinyl copolymerization</td>
</tr>
<tr>
<td>RAFT-SCVP</td>
<td>Reversible addition-fragmentation chain transfer self-condensing vinyl polymerization</td>
</tr>
<tr>
<td>RAFT-SCVCP</td>
<td>Reversible addition-fragmentation chain transfer self-condensing vinyl copolymerization</td>
</tr>
<tr>
<td>MI</td>
<td>Macroinitiator</td>
</tr>
<tr>
<td>CTA</td>
<td>Chain transfer agent</td>
</tr>
<tr>
<td>MWD</td>
<td>Molecular weight distribution</td>
</tr>
<tr>
<td>PRE</td>
<td>Persistent radical effect</td>
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<tr>
<td>Acronym</td>
<td>Full Form</td>
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<tr>
<td>---------</td>
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</tr>
<tr>
<td>DB</td>
<td>Degree of branching</td>
</tr>
<tr>
<td>SCROP</td>
<td>Self-condensing ring-opening polymerization</td>
</tr>
<tr>
<td>RCP</td>
<td>Radical copolymerization</td>
</tr>
<tr>
<td>FRCP</td>
<td>Free radical copolymerization</td>
</tr>
<tr>
<td>CRCP</td>
<td>Controlled radical copolymerization</td>
</tr>
<tr>
<td>SCVCP</td>
<td>Self-condensing vinyl copolymerization</td>
</tr>
<tr>
<td>MTEMPO</td>
<td>4-Methacryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxy</td>
</tr>
<tr>
<td>STEMPO</td>
<td>4-(4′-Vinylphenylmethoxy)2,2,6,6-tetramethyl-1-piperidinyloxy</td>
</tr>
<tr>
<td>CMS</td>
<td>p-(Chloromethyl)styrene</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2′-Bipyridine</td>
</tr>
<tr>
<td>nBA</td>
<td>n-Butyl acrylate</td>
</tr>
<tr>
<td>CysMA</td>
<td>Cysteine methacrylate</td>
</tr>
<tr>
<td>dNbpy</td>
<td>4,4′-Dinonyl-2,2′-dipyridyl</td>
</tr>
<tr>
<td>DTT</td>
<td>Dithiothreitol</td>
</tr>
<tr>
<td>OEGMA</td>
<td>Oligo(ethylene glycol) methyl ether methacrylate</td>
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<tr>
<td>Dh</td>
<td>Hydrodynamic size</td>
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<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<tr>
<td>SEC</td>
<td>Size exclusion chromatography</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
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</tr>
<tr>
<td>MALLS</td>
<td>Multi-angle laser light scattering</td>
</tr>
<tr>
<td>NaAs</td>
<td>Sodium ascorbate</td>
</tr>
<tr>
<td>ROMP</td>
<td>Ring opening metathesis polymerization</td>
</tr>
<tr>
<td>AIBN</td>
<td>2,2’-Azobisisobutynitrile</td>
</tr>
<tr>
<td>HEMA</td>
<td>2-Hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>GMA</td>
<td>Glycidyl methacrylate</td>
</tr>
<tr>
<td>EDC-HCl</td>
<td>4-3-(3-Dimethylaminopropyl)-1-ethyl-carbodiimide hydrochloride</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-(Dimethylamino) pyridine</td>
</tr>
<tr>
<td>V-40</td>
<td>1,1’-Azobis(cyclohexanecarbonitrile)</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>MeO-PEG-OH</td>
<td>Poly(ethylene glycol) methyl ether</td>
</tr>
<tr>
<td>TTC-CTA</td>
<td>Trithiocarbonate chain transfer agent</td>
</tr>
<tr>
<td>PEG-azo</td>
<td>PEG-labelled thermal azo initiator</td>
</tr>
<tr>
<td>BIEM</td>
<td>2-(2-Bromoisobutyryloxy) ethyl methacrylate</td>
</tr>
<tr>
<td>HEA</td>
<td>2-Hydroxyethyl acrylate</td>
</tr>
<tr>
<td>4VP</td>
<td>4-Vinyl pyridine</td>
</tr>
<tr>
<td>MAA</td>
<td>Methacrylic acid</td>
</tr>
<tr>
<td>MCTA</td>
<td>Macro chain transfer agent</td>
</tr>
<tr>
<td>MNP</td>
<td>Hybrid magnetic nanoparticle</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>Dimethylaminoethyl methacrylate</td>
</tr>
<tr>
<td>SI-ATRP</td>
<td>Surface-initiated atom transfer radical polymerization</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>APTES</td>
<td>3-Aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethoxysilane</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>HEMTETA</td>
<td>1,1,4,7,10,10-Hexamethyltriethylenetetramine</td>
</tr>
<tr>
<td>PH-PTZ</td>
<td>10-Phenylphenothiazine</td>
</tr>
<tr>
<td>BIBB</td>
<td>α-Bromoisobutyryl bromide</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
</tbody>
</table>
CHAPTER 1:
INTRODUCTION

1.1 Polymer architectures and controlled radical polymerization (CRP)

Synthetic polymers that comprise precise design, synthesis, processing, and characterization suitable for targeted applications have been considerably developed within the last few decades.\textsuperscript{1,2} The more demanding materials to face challenges in diversified environments and fields generated new directions in fundamental and applied polymer research to design and synthesize polymeric materials with controlled chemical compositions, molecular weights and molecular weight distributions (MWD), site-specific functionalities, and architectures. Individual macromolecules can be prepared in the shapes of branches, stars, combs, bottlebrushes, core-shells, rings, and networks.\textsuperscript{2} With the advantage of versatile polymerization methods, diversified monomers carrying various functionalities could be easily and precisely installed into macromolecules to provide targeted properties. Macromolecular engineering enables the development of numerous advanced polymeric materials that are needed in fields as diverse as coatings and adhesives, electronics, medicine and cosmetics, environment, and others.\textsuperscript{1} Macromolecular engineering resembles total synthesis of natural products, where the entire macromolecule is accurately designed to provide the desired properties and a sequence of synthetic steps is used to create a specific polymer.
architecture with desired placement of functional groups. Branching is the main tool for
development of polymeric architectures which could occur randomly or reactions may
be designed to target on specific architectures. A polymer's architecture affects many of
its physical properties including viscosity, solubility, and glass transition temperature.
Over the past decades, chemists have continuously explored novel synthetic approaches
for the preparation of functional polymers and materials with improved properties
which is associated to the polymer structures and architectures. Various reactions in the
field of organic chemistry have been applied in polymer chemistry, which has led to the
development of living ionic or coordination polymerization, where chain-breaking
reactions such as transfer or termination could be eliminated, but at the expense of
exhausting purification to eliminate any impurities from the polymerization medium. On
the other hand, nearly half of all polymers are produced by conventional free radical
polymerization (FRP) under more facile conditions. The commercial success of FRP can
largely be attributed to the unique features of this technique, including an extensive
range of vinyl monomers, their facile copolymerization, the benign reaction conditions,
and the very minimal requirements for purification of monomers and solvents. However,
control over molecular structure in a FRP is essentially impossible because radicals are
very reactive intermediates and their lifetime is less than 1 s. It is very challenging to
execute control over macromolecular structures during such a short time. On the other
hand, with the development of living polymerizations in the 1950s, these challenges
have been solved by using living ionic polymerization techniques. However, ionic
polymerization techniques are not suitable for the polymerization of a wide range of
functional vinyl monomers, mainly due to the incompatibility of the growing polymer chain end (anion or cation) with numerous functional groups and the requirement of stringent reaction conditions. Synthetic polymer chemists sought to develop new polymerization strategizes to overcome these limitations and combine the chemical robustness of conventional FRP with a high level of control over polymer composition and architecture. Consequently, the field of CRP has witnessed an explosive growth in the past two decades and has enabled the synthesis of a large variety of well-defined (co)polymer structures as depicted in Scheme 1.1.

![Polymer architectures](image)

**Scheme 1.1.** Polymer architectures.

All CRPs proceed through the same radical mechanism as a FRP. However, in contrast to FRP, the fundamental features of CRPs include fast initiation and creation of a dynamic equilibrium between a low concentration of propagating radicals and a large amount of dormant species. This concept minimizes the contribution of chain breaking
reactions and provides structural control over the polymers. Three different mechanisms of reversible activation are used to provide a CRP, they are: 1) dissociation-combination, represented by nitroxide-mediated polymerization (NMP)\(^3,4\) or organometallic radical polymerization; 2) a catalyzed atom transfer, represented by atom transfer radical polymerization (ATRP);\(^5,6\) and 3) degenerative chain transfer, represented by iodine mediated polymerization or reversible addition-fragmentation chain transfer (RAFT) polymerization.\(^7,8\) During these CRP processes, active radicals either undergo a reversible activation/deactivation process (e.g., ATRP), or participate in a degenerative transfer reaction (e.g., RAFT) to assure simultaneous growth of all chains.

Scheme 1.2. General schemes of NMP, ATRP and RAFT polymerization processes.
In NMP, the dormant species is cleaved by a thermal or photochemical stimulus to produce the stable free radical and the active propagating radical (Scheme 1.2A). The ATRP process is kinetically similar to NMP, except that the activation process includes the participation of both a dormant species and a catalyst-based activator, a lower oxidation state metal complex. The higher oxidation state metal complex formed in this activation procedure functions as the deactivator (Scheme 1.2B). Both NMP and ATRP are controlled by the persistent radical effect (PRE),\textsuperscript{1,9} which describes the procedure for self-regulation of the concentration of active radical. The difference between NMP and ATRP is that stoichiometric amount of mediating agent (e.g., nitroxide) is required to cap all dormant chains in the NMP system. In contrast, the amount of transition metal catalyst added to an ATRP system can be sub-stoichiometric because the catalytic process in ATRP employs an atom as capping group, which transfers between growing chains and a redox active catalyst. The RAFT polymerization process is a degenerative chain transfer reaction and is not based on the PRE (Scheme 1.2C). Its overall kinetics and polymerization rate resemble a conventional FRP process with slow initiation and fast termination reactions. However, the chain transfer agent employed to provide control is present at a much higher concentration than the radical initiator and quickly exchanges a group/atom among all growing chains. Thus, the transfer agent plays the role of the dormant species to provide control over molecular weights and dispersity. Since the invention of various CRP techniques, they have been constantly improved and applied to the preparation of well-defined polymers with
controlled chemical compositions, molecular weight and MWD, chain sequence distribution, functionalities and topologies.

1.2 Synthesis of hyperbranched polymers via radical polymerization

In the 1980s, highly branched polymers, also named dendritic polymers, were reported, and gradually became one of the most interesting areas of polymer science and engineering. Dendritic polymers include dendrimers which have perfect branched topologies with the degree of branching (DB) of 1.0 (calculated according DB = (D+T)/(D+L+T), where D, L and T are the fractions of dendritic, linear, and terminal units in the hyperbranched polymers) and hyperbranched polymers which exhibits a random and irregular branched configuration with lesser DB, normally ranging from 0.4 to 0.6. Generally, step-by-step synthesis, purification, protection, and deprotection are needed for accessing dendrimers with controlled molecular structures. In contrast to the tedious synthesis of dendrimers, HPBs offer a facile and efficient on-pot polymerization which leads to more promising industrial application with low producing cost and easy scale-up. Several strategies for the preparation of hyperbranched polymers are currently employed. Such as polymerization of a monomer containing one A functional group and two or more B functional groups capable of reacting with A (AB-f-type monomer, f≥2), polymerization of functionally symmetric monomer pairs of A_2 and B_3 monomers, polymerization of asymmetric monomer pairs of AA’ and B’B_2 monomers, self-condensing ring-opening polymerization (SCROP), radical copolymerization (RCP) of a monovinyl monomer and a cross-linker, and SCVP. So far, the most common method is the polymerization of nonvinyl AB_f monomers which involves typical features.
of a step-growth reaction of multifunctional monomers to form hyperbranched polymers. However, the limited commercial availability of functionally AB\textsubscript{r} type monomers has precluded their industrial implementation.\textsuperscript{19} Tremendous effort were utilized to tame this challenge with satisfactory results, such as polymerization of symmetric monomer pairs of A\textsubscript{2} and B\textsubscript{3} monomers,\textsuperscript{20,21} polymerization of asymmetric monomer pairs of AA’ and B’B\textsubscript{2},\textsuperscript{22-24} and multi-component methodology of polymerizing A\textsubscript{2}, C\textsubscript{2} and B\textsubscript{3}.$^{25}$ On the other hand, as the mostly commercial available monomer, vinyl monomers are extensively used in producing hyperbranched polymers via radical polymerization. So far, RCP of vinyl monomer and cross-linker and SCVP of AB* inimers (containing initiator fragment B* and monomer vinyl group A in one molecule) are the mainly used radical polymerization for hyperbranched polymer synthesis.

1.2.1 Synthesis of hyperbranched polymers via radical copolymerization (RCP) of a monovinyl monomer and a cross-linker

One-batch RCP of a monovinyl monomer and a cross-linker produces branched polymers or gels depend on polymerization degree comparing to the gelation point. The pendant vinyl groups in the polymer chains are generated by the incorporation of free cross-linker and consumed via their reaction with propagating radicals to produce an “X” shaped cross-linkage, from which four polymer chains radiate out as shown in Scheme 1.3. Both of FRP and CRP have been used to produce branched structures via this method, named FRCP and CRCP respectively, but FRCP so far could only produce inhomogeneous ill-defined structures due to its intrinsic intramolecular cyclization
behavior in comparison with CRCP.\textsuperscript{1} In contrast to the conventional FRCP technique, CRCP techniques have several advantages when targeting the preparation of more homogeneous hyperbranched polymers, due to the fast initiation and quick reversible deactivation reactions. The dynamic equilibrium in CRCP ensures that only a few monomer units are incorporated into the polymer chains in every activation/deactivation cycle. During the long “dormant” period, the polymer chains cannot propagate, but can diffuse and relax, which results in the probability of reaction of each vinyl species: monomer, cross-linker or pendant vinyl group, is statistically determined by their concentration.\textsuperscript{1} Thus, the application of CRCP techniques\textsuperscript{15,16,26-32} results in a more homogeneous incorporation of branching points into the soluble branched copolymers, as compared to polymers synthesized by FRP methods from similar concentrations of comonomers. Although structure control could be improved through CRCP, it is still tricky to produce hyperbranched polymers because of the challenge of gelation and structure control. Due to the adjustable molar ratio of cross-linker to initiator and the statistical distribution of cross-linkage among the primary chains, gelation occurs in the system when the average number of cross-linkage per primary chain reaches a critical value. In other words, the reaction has to be stopped before the gel point if soluble branched polymers are targeted. In addition, due to the trend of easy gelation, the monomer/cross-linker ratio has to be high which makes the DB lower comparing to other polymerization methods.
1.2.2 Synthesis of hyperbranched polymers via controlled radical self-condensing vinyl polymerization (CR-SCVP)

Fréchet et al. firstly reported hyperbranched polymers synthesized from inimers through a cationic SCVP mechanism\textsuperscript{18} and this discovery enabled the use of vinyl monomers for a one-pot synthesis of hyperbranched polymers with AB\textsuperscript{*} inimers. In an ideal SCVP process, living polymerization systems are preferred in order to avoid cross-linking reactions and gelation caused by chain transfer or recombination reactions. By copolymerizing AB\textsuperscript{*} inimers with conventional monomers, the SCVP technique was extended to self-condensing vinyl copolymerization (SCVCP). SCVP/SCVCP can be achieved by a variety of polymerization techniques depending on the nature of the initiating group. There have been examples of cationic polymerization,\textsuperscript{18,33} anionic polymerization,\textsuperscript{34-42} photo-mediated radical polymerization of polymerizable “iniferter” monomers,\textsuperscript{43-48} group transfer,\textsuperscript{49-51} ATRP,\textsuperscript{52-81} NMP\textsuperscript{82-84} and RAFT polymerization.\textsuperscript{7,40,46,85-}
As mentioned in the previous discussion, ionic “living” polymerizations’ application is limited by their incompatibility with many functional groups plus the stringent reaction conditions. On the other hand, the latter three CRPs offer a good solution to this challenge which resulted in more applications.

1.2.2.1 Synthesis of hyperbranched polymers by nitroxide-mediated radical self-condensing vinyl polymerization (NMR-SCVP)

As the first invented CRP technique, NMP was the first CRP applied in CR-SCVP. Hawker and Fréchet reported the first synthesis hyperbranched polymer using a NMR-SCVP approach (Scheme 1.4). In this case, a styrenic AB* inimer was functionalized with nitroxide linked to a substituted benzylic carbon atom. After 72 h reaction time, hyperbranched polymer with a number-averaged molecular weight \( M_n = 6000 \), a dispersity \( M_w/M_n = 1.40 \), and a \( T_g \) of 45 °C was produced without gelation. The produced hyperbranched polymer was further utilized as macroinitiator (MI) for a second-step chain extension to allow hyperbranched star (hyperstar) polymers and a \( M_n = 300,000 \) \( (M_w/M_n = 4.35) \) was successfully prepared. The presence of cleavable branching linkages (benzyl ether groups) in the hyperbranched polymers were also utilized to prove the presence and nature of the branching in hyperstar polymer. Linear polymer with \( M_n = 65,000 \) \( (M_w/M_n = 1.57) \) was obtained as result of the degradation of the hyperbranched polymer core. This is the first example of hyperstar polymer synthesis which opened the gate for synthesis of high-arm-density star polymers via chain extension of MIs.
Scheme 1.4. Homopolymerization of an alkoxyamine inimer by NMR-SCVP to form a hyperbranched polymer.

Polymerizable nitroxide, such as 4-methacryloyloxy-2,2,6,6-tetramethyl-1-piperidinylxoxy (MTEMPO) and 4-(4’-vinylphenylmethoxy)2,2,6,6-tetramethyl-1-piperidinylxoxy (STEMPO)\(^\text{84,90}\) (Scheme 1.5) were also utilized to introducing branching points into the polymers. The branch points of the hyperbranched polymers can undergo thermally reversible homolysis/recombination reactions. However, the nitroxide is mediating the polymerization to maintain “living” characteristic without functioning as a real initiating site as in the imimers.

Scheme 1.5. Structure of polymerizable nitroxides: MTEMPO and STEMPO.
While NMP has been used in the preparation of a wide variety of interesting polymer structures and has key advantages in simplicity, monomer compatibility, and polymer purity, it continues to suffer from three main challenges: 1) slow polymerization kinetics that require high temperature and lengthy polymerization time; 2) the inability to easily control the polymerization of methacrylate monomers due to side reactions and/or slow recombination of the polymer radical with nitroxide; and 3) synthetic difficulties associated with nitroxide and alkoxyamine synthesis that have generally limited studies to a few commercially available systems or to those carried out by synthetically focused research groups. 

1.2.2.2 Synthesis of hyperbranched polymers via atom transfer radical self-condensing vinyl polymerization (ATR-SCVP)

The first ATR-SCVP was reported by Matyjaszewski et al. using commercially available, p-(chloromethyl)styrene (CMS), in the presence of Cu(I) and 2,2’-bipyridine (bpy)\textsuperscript{53} (Scheme 1.6 A). Scheme 1.6 B illustrates the competition between the propagation and deactivation reactions in the ATRP of B* inimer, which is critical to mediate the branching process.
Scheme 1.6. A) Homopolymerization of CMS by ATR-SCVP to form a hyperbranched polymer. B) Dynamic exchange process during ATRP of inimer\(^{125}\). AB\(^*\) and B\(^*\) represent propagating radicals.

AB* inimers used in ATR-SCVP and ATR-SCVCP so far are listed in Table 1.2. Three types of AB* inimers in term of polymerizable vinyl group (A group) could be found in published artciles covering 1) acrylate inimers; 2) methacrylate inimers; and 3) styrenic inimers. On the other end of these AB* inimers, all of them contain alkyl halide groups: either alkyl bromide or alkyl chlorlide which generally employed Cu-based catalyst for initiating ATRP. A variety of acrylate AB* inimers have been reported, including AB*1-9.
as shown in Table 1.2. The significant influence of solubility of the deactivator which are closely related to the concentration of Cu(II), on the topology of the resulting polymers has also been reported. However, methacrylate AB* inimers AB*13 and AB*14 could not be successfully polymerized by such Cu-based ATRP despite variations in ligand and temperature mainly due to the easy radical coupling from the tertiary radical sites forming an excess amount of deactivating Cu(II) species. For the preparation of hyperbranched methacrylates, Cu-based ATRP with addition of Cu (0) for AB*13 and AB*14, Ni-based controlled radical polymerization for AB*13, have been employed to achieve better results. It is worthy to mention that the accumulation of deactivator of Cu(II) in the solution or bulk system was solved by an hetergenerous microemulsion polymerization system reported by Gao et al. who achieved high molecular weight with polymerization of AB*13 inimer due to the partitioning of Cu (II) into the aqueous phase. So far, styreneic AB* inimers were not popularly used in ATR-SCVP to produce hyperbranched polymers. AB*10 and AB*11 as shown in Table 1.2 are two representative inimers and AB*10 is an unsymmetrical inimer which offered tunable structures from liner to hyperbranced under different temperatures and ligands.
TABLE 1.1.

AB* INIMERS USED IN ATR-SCVP

<table>
<thead>
<tr>
<th>AB* ref.</th>
<th>Structure</th>
<th>AB* ref.</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB*1&lt;sup&gt;54-56&lt;/sup&gt;</td>
<td><img src="image1.png" alt="Structure AB*1" /></td>
<td>AB*11&lt;sup&gt;71&lt;/sup&gt;</td>
<td><img src="image2.png" alt="Structure AB*11" /></td>
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<tr>
<td>AB*2&lt;sup&gt;4-6&lt;/sup&gt;</td>
<td><img src="image3.png" alt="Structure AB*2" /></td>
<td>AB*12&lt;sup&gt;125,128,129&lt;/sup&gt;</td>
<td><img src="image4.png" alt="Structure AB*12" /></td>
</tr>
<tr>
<td>AB*3&lt;sup&gt;63&lt;/sup&gt;</td>
<td><img src="image5.png" alt="Structure AB*3" /></td>
<td>AB*13&lt;sup&gt;62,127&lt;/sup&gt;</td>
<td><img src="image6.png" alt="Structure AB*13" /></td>
</tr>
<tr>
<td>AB*4&lt;sup&gt;68&lt;/sup&gt;</td>
<td><img src="image7.png" alt="Structure AB*4" /></td>
<td>AB*14&lt;sup&gt;126&lt;/sup&gt;</td>
<td><img src="image8.png" alt="Structure AB*14" /></td>
</tr>
<tr>
<td>AB*5&lt;sup&gt;59&lt;/sup&gt;</td>
<td><img src="image9.png" alt="Structure AB*5" /></td>
<td>AB*15&lt;sup&gt;60&lt;/sup&gt;</td>
<td><img src="image10.png" alt="Structure AB*15" /></td>
</tr>
<tr>
<td>AB*6&lt;sup&gt;64&lt;/sup&gt;</td>
<td><img src="image11.png" alt="Structure AB*6" /></td>
<td>AB*16&lt;sup&gt;69&lt;/sup&gt;</td>
<td><img src="image12.png" alt="Structure AB*16" /></td>
</tr>
<tr>
<td>AB*7&lt;sup&gt;58&lt;/sup&gt;</td>
<td><img src="image13.png" alt="Structure AB*7" /></td>
<td>AB*17&lt;sup&gt;81&lt;/sup&gt;</td>
<td><img src="image14.png" alt="Structure AB*17" /></td>
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<tr>
<td>AB*8&lt;sup&gt;60&lt;/sup&gt;</td>
<td><img src="image15.png" alt="Structure AB*8" /></td>
<td>AB*18&lt;sup&gt;125,127-129&lt;/sup&gt;</td>
<td><img src="image16.png" alt="Structure AB*18" /></td>
</tr>
<tr>
<td>AB*9&lt;sup&gt;73&lt;/sup&gt;</td>
<td><img src="image17.png" alt="Structure AB*9" /></td>
<td>AB*19&lt;sup&gt;127,129-131&lt;/sup&gt;</td>
<td><img src="image18.png" alt="Structure AB*19" /></td>
</tr>
<tr>
<td>AB*10&lt;sup&gt;79&lt;/sup&gt;</td>
<td><img src="image19.png" alt="Structure AB*10" /></td>
<td>AB*20&lt;sup&gt;127,129-131&lt;/sup&gt;</td>
<td><img src="image20.png" alt="Structure AB*20" /></td>
</tr>
</tbody>
</table>
Most of the reported ATR-SCVP of AB* inimers have been done in bulk or solution. The homogeneous reaction medium causes unconfined polymer-polymer reactions throughout the reactor that leads to polymers with poorly defined structure. To tame this challenge, Gao et al. reported the application of confined space, i.e., microemulsion, to regulate the synthesis of hyperbranched polymers by conducting one-pot ATR-SCVP of AB* inimers (Scheme 1.7).\textsuperscript{127} The segregated space in the microemulsion successfully confined the polymer-polymer reactions within discrete polymerizing nanoparticles. Consequently, the obtained hyperbranched polymers showed narrow molecular weight distribution and hydrodynamic size similar to that of nanoparticles.

![Scheme 1.7. Polymerization of inimers in microemulsion.\textsuperscript{127}](image)

\textsuperscript{127}
1.2.2.3 Synthesis of hyperbranched polymers by reversible addition-fragmentation chain transfer self-condensing vinyl polymerization (RAFT-SCVP)

Chain transfer agent (CTA), usually a thiocarbonylthio compound with a structure as \(Z(C=\text{S})SR\), is the key component in RAFT process which mediates the equilibrium between active and dormant chains. The \(Z\)-group activates the thiocarbonyl double bond and provides stability to the intermediate adduct formed when radicals add to the CTA, while the \(R\)-group is a good leaving group capable of reinitiating RAFT polymerization after fragmentation. In RAFT-SCVP, as similar as an \(AB^*\) inimer in ATRP SCVP, a polymerizable vinyl group (A group) is installed into the CTA structure (\(B^*\) group) on either \(R\)-group or \(Z\)-group side. This allows two methods including 1) \(R\) method with vinyl group installed on the \(R\) group and 2) \(Z\) method with vinyl group installed on \(Z\) group (Scheme 1.8) for hyperbranched polymer preparation. In the published work, polymerizable CTA was usually referred as \(AB^*\) inimer. However, this \(B^*\) group is different from that in ATRP and NMP \(AB^*\) inimer since it is not an initiator and it needs external radical source to cleave the -S-R- bond to generate the \(B^*\). This makes the term inimer not accurate to describe it while polymerizable chain transfer monomer (transmer) would be referred for later discussion. However, as a special type of transmer, iniferter monomer, is able to generate radical under the activation of light and iniferter transmer will be used to differentiate these two types of transmers for discussion.
So far, most of the RAFT SCVPs were conducted by a copolymerization process with various functional monovinyl monomers. The so-called RAFT self-condensing vinyl copolymerization (RAFT-SCVCP) makes it easy to tune the DB and introduce certain functionalities. Only a couple examples of homo RAFT-SCVP could be found. The first homopolymerization of transmer was reported in 2011 by Zhao and coworkers who used S-(4-vinyl)benzyl S'-propyltrithiocarbonate (VBPT) to prepare homo-hyperbranched polymer as an control experiment with the intention to compare the solution behavior of branched copolymers obtained by RAFT-SCVCP. A thorough literature research within the best of our knowledge indicates that RAFT homopolymerization of transmers when
using thermal initiators as radical sources could only produce low-molecular-weight hyperbranched polymers. Several groups have reported results for RAFT homopolymerization of transmers with only relatively low molecular weights achieved: these examples includes $M_n = 24,700$ from the Zhao group, $M_n = 8,740$ from the Sumerlin group, and $M_n < 1,000$ from the Poly group. On the other hand, Ishizu and Tanaka reported the photo-polymerization of iniferter transmer and produced hyperbranched polymers with molecular weight above 100k although no detailed polymerization kinetics and degree of branching were studied. Since then, there was no homopolymerization of transmers until 2016 when our group reported a systematic study of homopolymerization of a trithiocarbonate transmer with intention to increase the molecular weight of homo-hyperbranched polymers. This article presents the first synthesis of high-molecular-weight hyperbranched polymers (over half a million) in the homopolymerization of transmer by applying a new initiation process to activate the alkyl trithiocarbonate to generate radicals without the use of thermal initiator or photoinitiation.

For the polymerization of transmers, most of them were conducted by RAFT-SCVCP with mono-vinyl functional monomers to produce the segmented hyperbranched polymers (SHBs). The addition of mono-vinyl monomers diluted the branching density and consequently lowers the DB in general. The first journal article of the RAFT-SCVCP was published in 2003 by Yang et al. who utilized RAFT-SCVCP to preparing hyperbranched polystyrene. The transmer structure was based on a styrenic dithioester transmer 2 (Table 1.2) with a 4-vinylphenyl as the Z-group. By introducing
the dithioester group into the branching point, it offers an advantage of preparing segmented hyperbranched copolymers through a two-step polymerization method. As shown in Scheme 1.9 B, one mono-vinyl monomer was copolymerized with transfer first, afterwards, the reactive CTA groups at each branch point allow insertion of second block at each branching point to generate branched block-copolymers. In contrast, a star-shaped copolymer would be produced if the hyperbranched polymers were made out of R method since the CTA groups are at the periphery of the hyperbranched polymers (Scheme 1.8A). This was utilized by Patrickios and coworkers to segmented amphiphilic hyperbranched polymers of styrene, 2-vinylpyridine, and 4-vinylpyridine through step-wise RAFT-SCVP. In comparison with NMR-SCVP and ATR-SCVP, which could only provide the star-shaped copolymers, RAFT-SCVP and RAFT-SCVCP offer more possibilities for polymer architectures development by designing the transmer structures. The two main limitations of this Z-approach were the steric hindrance to access the CTA functionalities and the potential weakness of the branch points. To solve this problem, Puskas and coworkers reported the first bulk polymerization of styrene with 4-vinylbenzyl dithiobenzoate which avoided introducing the CTA into the branching point (R method). Since then, the R method was utilized more frequently and diversified branched polymer structures were produced.

To achieve the uniform distribution of branches commonly envisioned for idealized depictions of hyperbranched polymers, similar reactivity between the polymerizable group of the transmer and the vinyl group of the comonomer is critical. Table 1.2 summarizes the transmers that have been prepared to date. While the first
transmers reported were strictly limited to styrenic polymerizable groups, new examples of transmers with acrylate/methacrylate polymerizable groups were developed over time. Moreover, trithiocarbonate transmers were developed, which increased the hydrolytic stability of the end group as compared to dithiobenzoates. This increased stability was crucial for successful chain extension to form star polymers. Xanthate-based transmers reported by both the Poly\textsuperscript{100} and Zhou\textsuperscript{102} groups were subsequently used to prepare hyperbranched poly(vinyl acetate). The development of these new transmers was crucial for this vinyl ester monomer, because poor control is achieved with other CTAs. In the case of iniferter transmers, the most common ones are usually the dithiocarbamate (DC) type. Photopolymerizations in benzene solution of 2-(N,N-diethylaminodithiocarbamoyl)ethyl methacrylate (DTCM) were carried out by Mori et al.\textsuperscript{45} via irradiation with UV light in a sealed glass ampoule under high vacuum at 20 °C.
### TABLE 1.2
TRANSMERS USED IN RAFT-SCVCP/RAFT-SCVCP

<table>
<thead>
<tr>
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<th>Structure</th>
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So far, the homopolymerization of transmers to targeting on a high molecular weight is still challenging with the employment of traditional thermal initiator though various adjustments of polymerization conditions have been tried.\textsuperscript{132} It is highly desired to find out the reason and provide a solution to help understating the RAFT-SCVP mechanism and achieve facile tunability of molecular weight of hyperbranched polymers, especially when targeting on a high molecular weight. The low molecular weight problem is rooted in the initiation mechanism of RAFT polymerization and the avoidance of external radical source, e.g., photopolymerization of iniferter transmers, could be the guidance for the solution of this problem. On the other hand, like other one-pot solution or bulk SCVP of AB\textsuperscript{*} inimers, the random polymer-polymer reaction makes the control over MWD extremely hard. The application of confined space, i.e., microemulsion, in the regulation of hyperbranched polymers produced from ATRP SCVP did provide a potential solution to this challenge.
1.3 Hyperstar polymers synthesized using hyperbranched polymers as macroinitiators (MIs) via CRP chain extension

![Diagram of Grafting from and Grafting onto](image)

Scheme 1.9. Schematic synthesis procedures of hyperstar polymers with “grafting from” and “grafting onto” methods.

Hyperstar polymers are core-shell structured star polymers developed with the advent of hyperbranched polymers, which represent an important category of soft nanomaterials. In general, core-shell structured hyperstar polymers are commonly prepared via one of the two well documented strategies: “grafting from” and “grafting onto” (Scheme 1.11). The “grafting from” method applies a terminal-functionalized hyperbranched polymer as core MI for the polymerization of monovinyl monomers using various CRP techniques, including ATRP, NMP, and RAFT polymerization, and anionic ROP. The “grafting onto” method utilizes efficient coupling reactions to tether a chain-end functionalized linear...
arm onto the terminal-functionalized hyperbranched polymer.\textsuperscript{153-157} Although both “grafting from” and “grafting onto” routes have advantages and limitations, the “grafting from” method in practice becomes more popular for preparation of densely grafted hyperstar polymers due to the less concern of steric hindrance involved in this method.\textsuperscript{158-160} So far, most of the hyperstar polymers are poorly defined from the dispersity point of view due to the ill-regulated MI structures which are normally produced from a one-pot solution polymerization. In addition, the current two-step polymerization procedure of grafting from method is usually carried out in solution and therefore complicated by the inevitable radical coupling reactions between two or more multifunctional star polymers.\textsuperscript{127} As a result, the hyperstar polymers have to be synthesized in a dilute solution and the polymerization is usually stopped at low monomer conversion. It is highly desired to develop a one-pot method that can produce hyperstar polymers at high monomer conversions without hyperstar-hyperstar coupling reactions to further expand the application of hyperstar polymers.

1.4 Thesis goals

The main object of this dissertation is the development of new methodologies for synthesis of hyperbranched polymers and hyperstar polymers with controlled structures and site-specific functionalities via CRP techniques. The main tools used to achieve this goal include CRP SCVP and chain extension CRP polymerization with solution and heterogeneous microemulsion/seeded emulsion polymerization. Hyperbranched polymers that synthesized in a one-pot solution polymerization via CRP
SCVP suffer from a poorly defined structure with broad MWD due to the random polymer-polymer combination. In addition, the hyperstar polymers made out of these hyperbranched polymers by simply chain extension polymerization in solution or bulk directly suffer from the poorly defined core structure which makes the control over hyperstar polymers structures a mission of impossible, let alone the existence of unavoidable star-star coupling side reaction which imposes an extra hindrance for a well-controlled structure. Current challenges in regulation of hyperbranched polymers and hyperstar polymers structure produced by CRP is mainly about the lack of tools to regulate structure, especially molecular weight and MWD. To solve these challenges, the implementation of confined space, e.g., microemulsion with narrowly distributed micelles provided a promising solution and it was applied in the regulation of hyperbranched polymers structures made out of ATRP SCVP. By segregating the polymerization of monomers within discrete micelles, the monomers within a confined space can react with each other completely without inter-space reaction to allow only one hyperbranched polymer per micelle, whose size, molecular weight, and dispersity will be closely dependent on the size and uniformity of the confined space. However, when applying this methodology in the RAFT SCVP process which offers more functionality and compatibility in comparison with ATRP, it was observed that only small polymer fractions could be obtained after pushing the transmer to the highest conversion with the initiation of AIBN initiator. No significant improvement was achieved with intensively varying the polymerization conditions. It is highly desired to find out the reason and seek solution to increase the molecular weight in the RAFT SCVP
which could be potentially utilized in microemulsion polymerization which requires a high molecular weight, i.e., over half a million. Meanwhile, regarding to the structure control over hyperstar polymers by using CRP chain extension through a two-step procedures, a noticeable limitation is that the second-step arm growth from the hyperbranched MI is carried out in solution and therefore complicated by the inevitable radical coupling reactions between two or more multifunctional star polymers. As a result, the hyperstar polymers have to be synthesized in a dilute solution and the polymerization is usually stopped at low monomer conversion. These limitations guided me to develop a one-pot method that can produce hyperstar polymers at high monomer conversions without hyperstar-hyperstar coupling reactions.

Development of synthetic routes for structural control over hyperbranched polymers and hyperstar polymers would not only help us understand these synthetic systems, but also provide us a unique advantage to access large amounts of functional polymer materials with well-defined structures. Such synthetic ease is a prerequisite for further study of the physical properties of these functional materials to explore their potential applications via broad collaboration with different research groups both within and outside University of Notre Dame. Many collaborative projects are either completed or actively underway using the functional hyperstar polymers to explore the use of the materials in different fields, including the application of degradable cationic hyperstar polymers to develop combinatorial therapy for triple negative breast cancer treatment via drug encapsulation and formulation in collaboration with Prof. Dipanjan Pan at UIUC, the development of excipient-free freeze-dryable unimolecular hyperstar polymers for
efficient siRNA silencing with Prof. Gang Han at the University of Massachusetts-Medical School, and the application of hierarchically hyperstar polymer as new solid polymer electrolyte for rechargeable lithium-ion battery in collaboration with Prof. Elaine Zhu at Wayne State University and Professor Susan Fullerton at the University of Pittsburgh.

1.5 References


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CHAPTER 2:

ONE-POT SYNTHESIS OF HYPERSTAR POLYMERS VIA SEQUENTIAL ATRP OF INIMERS AND FUNCTIONAL MONOMERS IN AQUEOUS DISPERSED MEDIA

2.1 Introduction

Core-shell structured star polymers that contain a highly branched polymer as core and densely grafted radiating arms, as termed “hyperstar” polymers, represent an important category of soft nanomaterials. The features of compact structure, globular shape and large surface area in a hyperstar polymer find it promising applications as a unimolecular container in various areas, such as catalysis, nanomedicines, and imaging diagnostics. In general, core-shell structured hyperstar polymers are commonly prepared via one of the two well documented strategies: “grafting from” and “grafting onto”. The “grafting from” method applies a terminal-functionalized hyperbranched polymer as core macroinitiator (MI) for the polymerization of monovinyl monomers using various controlled/“living” polymerization techniques, including ATRP, NMP, RAFT polymerization, and anionic ring-opening polymerization (ROP). The “grafting onto” method utilizes efficient

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coupling reactions to tether a chain-end functionalized linear arm onto the terminal-functionalized hyperbranched polymer.\textsuperscript{34-38} Although both “grafting from” and “grafting onto” routes have advantages and limitations, the “grafting from” method in practice becomes more popular for preparation of densely grafted hyperstar polymers due to the less concern of steric hindrance involved in this method.\textsuperscript{39-41}

To prepare structurally defined hyperstar polymers, a highly desired condition is the use of hyperbranched MIs that have low dispersity and high density of initiating groups. So far, both dendrimers\textsuperscript{42,43} and hyperbranched polymers\textsuperscript{22,44,45} have been used for synthesis of hyperstar polymers in the “grafting from” method. However, the tradeoff between dendrimers and hyperbranched polymers on their synthetic easiness and structural uniformity still remains as a challenge to produce hyperstar polymers with well-defined structures and in large quantities.

In 2012, our group developed new methods on the one-pot synthesis of hyperbranched polymer with high molecular weights, high degree of branching (DB) and low dispersity by using either confined space\textsuperscript{5,46} or chain-growth click polymerization of AB\textsubscript{2} monomers.\textsuperscript{47} Among them, the confined space method was able to produce uniform hyperbranched polymers by conducting the one-pot ATRP of AB* inimers in microemulsion. The obtained hyperbranched polymers that contained $10^2$-$10^3$ bromide initiating sites with dispersity ($M_w/M_n < 1.3$) were purified and subsequently used as MIs in a second-pot polymerization of functional monomers to synthesize hyperstar polymers.\textsuperscript{5} In these two-step procedures, a noticeable limitation is that the second-step arm growth from the hyperbranched MI is carried out in solution and therefore
complicated by the inevitable radical coupling reactions between two or more multifunctional star polymers. As a result, the hyperstar polymers have to be synthesized in a dilute solution and the polymerization is usually stopped at low monomer conversion. It is highly desired to develop a one-pot method that can produce hyperstar polymers at high monomer conversions without hyperstar-hyperstar coupling reactions.

In this contribution, we report the first synthesis of hyperstar polymers with high monomer conversion and low dispersity using a one-pot procedure. As shown in Scheme 2.1. Synthesis of hyperstar polymers via one-pot polymerization., structurally defined hyperbranched polymers were synthesized via one-pot activators generated by electron transfer (AGET)\(^{30,31}\) ATRP of inimers in microemulsion.\(^{5,47,48}\) At complete inimer conversion, the produced hyperbranched polymers without purification were directly used as MIs for chain extension via in situ polymerization of monomers with different polarities: hydrophobic \(n\)-butyl acrylate (\(n\)BA) and hydrophilic zwitterionic cysteine methacrylate (CysMA). In both cases, the production of hyperstar polymers was protected by steric segregation in the seeded emulsion polymerization of \(n\)BA or the electrostatic repulsion in the surface polymerization of CysMA. Consequently, well-defined hyperstar polymers were easily obtained at high monomer conversions with no detectable amount of hyperstar-hyperstar couplings.
Scheme 2.1. Synthesis of hyperstar polymers via one-pot polymerization.

2.2 Experimental

2.2.1 Materials

All chemicals and solvents, including 4,4'-dinonyl-2,2'-dipyridyl (dNbpy), CuBr₂, sodium ascorbate (NaAs), Sn(II) 2-ethylhexanoate, dithiothreitol (DTT), and polyoxyethylene(20) oleyl ether (Brij98), were purchased from Aldrich with the highest purity and used as received unless otherwise stated. 2-(2-Bromoisobutylryloxy) ethyl methacrylate (inimer 1),⁴⁹ and 2-((2-((3-methyl-2-oxobut-3-en-1-yl)xy)ethyl) disulfanyl)ethyl 2-bromo-2-methyl propanoate (inimer 2)⁵,⁴⁶ were synthesized according to reported methods. Monomers, including n-butyl acrylate (nBA,
≥ 99%) and oligo(ethylene glycol) methyl ether methacrylate (OEGMA<sub>300</sub>, M<sub>n</sub> = 300) were purified by passing through the column filled with basic aluminum oxide (Sorbent Technologies) to remove inhibitor. Synthesis of CysMA was according to a published report<sup>50</sup> using 3-(acryloyloxy)-2-hydroxypropyl methacrylate, L-cysteine and dimethylphenyl phosphine purchased from Aldrich.

2.2.2 Characterization

The hydrodynamic size (D<sub>h</sub>) and zeta potential (ζ) distribution of polymer samples were determined by dynamic light scattering (DLS) equipped with a Zetasizer Nano-ZS (He-Ne laser wavelength at 633nm) and an auto-titrator (Malvern Instruments, Malvern, UK). Nuclear magnetic resonance (NMR) spectroscopy was carried out on a Bruker DM × 400 spectrometer operated in the Fourier transform mode. After filtration through 0.45 µm PTFE filter, the polymer samples were separated by size exclusion chromatography (SEC) with tetrahydrofuran (THF) as mobile phase. The THF SEC was equipped with Polymer Standards Services (PSS) columns (guard, 10<sup>5</sup>, 10<sup>3</sup>, and 10<sup>2</sup> Å SDV columns) at 35 °C with THF flow rate = 1.00 mL/min, a differential refractive index (RI) detector (Wyatt Technology, Optilab T-rEX) using PSS WinGPC 7.5 software. The apparent molecular weights were calculated based on linear poly(methyl methacrylate) (PMMA) standards. The detectors employed to measure the absolute molecular weights of hyperbranched and hyperstar polymers in THF SEC were the RI detector and a multi-angle laser light scattering (MALLS) detector (Wyatt
Technology, DAWN HELEOS II) with the light wavelength at 658 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology with the $dn/dc = 0.084$ mL/g for all polymers. The molecular weight of zwitterionic hyperstar was characterized using the batch-mode MALLS with the value of $dn/dc = 0.159$ mL/g, determined via an off-line measurement of five polymer solutions with different concentrations (0.1 mg/mL, 0.5 mg/mL, 1.2 mg/mL, 3.0 mg/mL, 5.0 mg/mL).

2.2.3 Synthetic procedures

2.2.3.1 Synthesis of inimers

Synthesis of 2-(2-Bromoisobutyryloxy)ethyl methacrylate (inimer 1) and 2-((2-((3-Methyl-2-oxobut-3-en-1yl)xy)ethyl)disulfanyl)ethyl 2-Bromo-2-methyl propanoate (inimer 2). Two inimers (inimer 1 and inimer 2) were synthesized according to the literature procedures. Inimer 1: $^1$H NMR (CDCl$_3$ as solvent, $\delta$, ppm): 6.07 (1H, $CH_2=CH(CH_3)$), 5.52 (1H, $CH_2=CH(CH_3)$), 4.35 (4H, OCH$_2$CH$_2$O), 1.88 (3H, CH$_2=CH(CH_3)$), and 1.86 (6H, C(CH$_3$)$_2$Br); inimer 2: 500 MHz 1H NMR spectroscopy (CDCl$_3$ as solvent, $\delta$, ppm): 6.08 (1H, $CH_2=CH(CH_3)$), 5.53 (1H, $CH_2=CH(CH_3)$), 4.35 (4H, OCH$_2$CH$_2$O), 2.90 (4H, $CH_2S$), 1.95 (3H, CH$_2=CH(CH_3)$), and 1.90 (6H, C(CH$_3$)$_2$Br).
2.2.3.2 Synthesis of hyperbranched polymer HB1 and HB2 via AGET ATRP of inimers in microemulsion

All experimental procedures for synthesis of hyperbranched polymers (HB1 for hyperbranched polymer made from inimer1 and HB2 for hyperbranched polymers made from inimer 2) in microemulsion conditions were similar. A typical procedure on polymerization of inimer 1 with [inimer 1]_0/[CuBr₂]_0/[dNbpy]_0/[NaAs]_0 = 70/1/2/0.5 is briefly described. In a disposable test tube, dNbpy (10.6 mg, 0.026 mmol) and CuBr₂ (2.9 mg, 0.013 mmol) were mixed in 0.5 mL of DCM at 40 °C for half an hour before addition of inimer 1 (0.25 g, 0.90 mmol) to the mixture. After evaporation of the DCM at 40 °C, the mixture was added dropwise to a solution of 1 g Brij98 in 12 g water over 30 minutes to form a transparent microemulsion. Meanwhile, the temperature was slowly stepped up to 65 °C and stabilized for less than 10 minutes before injection of 0.10 mL of NaAs solution in water to reduce the Cu(II) species and initiate the polymerization. The reaction was stopped after 2 hours by exposure to air.

2.2.3.3 Synthesis of hyperstar polymers

The produced hyperstar polymers were designated as HS1-PnBA, HS1-PCysMA, HS1-POEGMA when using HB1 as MI, and HS2-PnBA, HS2-PCysMA, HS2-POEGMA when using HB2 as MI. Synthesis of HS1-PnBA and HS2-PnBA hyperstar polymers in a one-pot polymerization. The experimental procedures for synthesis of HS1-PnBA and HS2-PnBA are similar. After the first-step synthesis of HB1 and HB2 hyperbranched core were carried out according to the before described procedures. The microemulsions of the
first-step product were cooled to room temperature before nBA (2.6g, 21 mmol) was added into the microemulsion. Microemulsion with added nBA monomer was stirred gently under N₂ bubbling for 30 min to emulsify nBA into the latexes before elevating the temperature to 60 °C and injecting 0.5 mL of deoxygenated 0.10 mL NaAs water solution into the system. In the syntheses, samples were withdrawn periodically from the reactions for GC measurements of monomer conversions, DLS measurements of $D_h$ and SEC measurements of molecular weights. After reaction, the emulsions were broken by adding THF and precipitated into methanol. The products were collected by centrifugation and purified by dissolving in THF and precipitating in methanol three times. Synthesis of HS1-PCysMA and HS2-PCysMA hyperstar polymers in a one-pot polymerization. The first step of synthesizing HB1 and HB2 as MI were the same as aforementioned procedures. The hyperstar polymer with PCysMA arms was synthesized with $[\text{Br}]_0/[\text{CysMA}]_0/[\text{CuBr}_2]_0/[\text{dNbpy}]_0/[\text{NaAs}]_0 = 70/3500/1/2/0.5$ at room temperature. The zwitterionic CysMA dissolved in deionized (DI) water was injected into the microemulsion before tuning the pH to the desired value using a 0.5 M NaOH or HCl aqueous solution. The microemulsion system at room temperature was then bubbled with N₂ for 30 minutes before the addition of 0.5 mL of deoxygenated NaAs aqueous solution into the system. DLS measurements of $D_h$ was tracked and samples were taken under different time intervals for $^1$H NMR measurement for monomer conversion tracking. After desired conversion was achieved, the polymerization was stopped by opening to the air. Finally, the hyperstar polymers were purified through precipitating to acetone up to three times and air dried.
2.2.3.4 Control experiments

Water-soluble non-charged monovinyl monomer OEGMA$_{300}$ was used to prove the steric or electrostatic protection is essential to avoid the star-star coupling reaction during the in-situ chain extension polymerization. The OEGMA$_{300}$ was added to the HB1 microemulsion for polymerization with $[\text{Br}]_0 : [\text{OEGMA}_300]_0/[\text{CuBr}_2]_0/[\text{dNbpy}]_0/[\text{NaAs}]_0 = 70/3500/1/2/0.5$ at $45^\circ$C. The microemulsion with HB1 latex with added OEGMA$_{300}$ was bubbled with $\text{N}_2$ for 30 minutes before the injection of the 0.5 mL of deoxygenated NaAs solution. Samples were withdrawn periodically from the reactions for $^1\text{H}$ NMR measurements of monomer conversions until the gelation occurred. Hyperbranched HB1 as MI for normal ATRP of nBA in bulk. The bulk polymerization of nBA with HB1 as MI was conducted with $[\text{Br}]_0/[\text{nBA}]_0/[\text{CuBr}_2]_0/[\text{dNbpy}]_0/[\text{Tin(II) 2-ethylhexanoate}]_0 = 70/2100/1/2/0.25$ at $60^\circ$C. HB1 (0.2 g), dNbpy (8.2 mg), CuBr$_2$ (2.3 mg) nBA (2.3 g), and anisole (45µL) were added to a schlenk flask. The mixture was sealed and deoxygenated by three freeze-pump-thaw cycles. In the frozen state, Tin(II) 2-ethylhexanoate (1.1 mg) was injected by micro syringe under protection of $\text{N}_2$ flow. The flask was then subjected to two additional freeze-pump-$\text{N}_2$ backfilling cycles before thawed at room temperature. Under protection of flowing $\text{N}_2$, samples were taken out of the reactor at five timed intervals to determine the monomer conversion using GC. The polymerization was stopped by exposure to air after gelation occurred.
2.3 Results and Discussion

2.3.1 Synthesis of hyperbranched polymers

Two hyperbranched polymers (HB1 and HB2, Table 2.2) that have high molecular weight, low dispersity, high DB, and high fraction of bromine functionality were synthesized via one-pot AGET ATRP of inimers 1 and 2 in microemulsion (Scheme 2.1). Both polymerizations were carried out using similar conditions ([inimer]₀/[CuBr₂]₀/[dNbpy]₀/[NaAs]₀ = 70/1/2/0.5 with 0.2 g of inimer and 1 g of Brij98 in 12 mL water) and finished within 2 hours at complete inimer conversions (Table 2.2). After purification, the hyperbranched polymers, HB1 and HB2, were characterized using the inverse gated decoupled $^{13}$C NMR spectroscopy as shown in Figure 2.1 to determine the DB as 0.30 and 0.38, respectively, based on literature reported method. Calculation of the DB of HB1 and HB2 was based on the integration of peaks: $\delta (30.5-31) = 2N_{B^*} + N_{A^*}$ and $\delta (55.3-55.8) = N_{B^*}$ in the spectrum of Figure 2.1A for HB1, $\delta (30.3-31.3) = 2N_{B^*} + N_{A^*}$ and $\delta (55.1-55.9) = N_{B^*}$ in the spectrum of Figure 2.1B for HB2. For the HB1, since the conversion of methacrylate groups in inimer 1 was >98% after polymerization, a complete conversion of conv. = 1 was applied to simplify the calculation. Without considering intermolecular cyclization and radical termination, the number of $A^*$ subunit equals the number of $b$ ($N_{A^*} = N_b = 0.23$). Using this relationship, the number fraction of $B^*$ subunit was determined as $f_{B^*} = \frac{N_{B^*}}{N_{B^*} + N_b} = 0.813$, which was then used to calculate the reactivity ratio ($r = \frac{k_{A^*}}{k_{B^*}} = \frac{conv_{A^*} + f_{B^*}^{-1}}{-\ln f_{B^*} + f_{B^*}^{-1} = 40.6}$) and a DB = 0.30 was calculated. For the HB2, $N_{A^*} = N_b = 0.34$, ...
\[ f_{B^*} = \frac{N_{B^*}}{N_{B^*} + N_b} = 0.75, \text{ and } r = \frac{k_{A^*}}{k_{B^*}} = \frac{\text{conv}_{A^*} + f_{B^*} - 1}{-\ln f_{B^*} + f_{B^*} - 1} = 19.1 \text{ which indicated the DB} = 0.38 \text{ for HB2.}

In addition, the NMR results indicate that both HB1 and HB2 polymers preserved very high bromine chain-end functionality (~100%) with detailed calculation as followed: In the structure of HB1, bromines are located at initiating sites from reacted double bond (A*) and unreacted initiating sites (B*). The carbon atoms in the ethylene (C5 in Figure 2.1A) or the methylene linkers (C5 and C6 in Figure 2.1B) were used as internal reference for the calculation. \( \text{Area}_{\delta(30.5-31)} = 2N_{B^*} + N_{A^*} = 2.23 \)

\[
\begin{align*}
\text{Area}_{\delta(30.5-55.8)} &= N_{B^*} = 1.0 \\
N_{A^*} &= 2.23 - 2 \times 1.0 = 0.23 \\
N_{Br \text{ in polymer}} &= N_{A^*} + N_{B^*} = 1.0 + 0.23 = 1.23 \\
\text{Area}_{\delta(62.2-63.7)} &= 2N_{Br \text{ theoretical}} = 2.31 \\
N_{Br \text{ theoretical}} &= 2.31/2 = 1.15 \\
\text{Fraction of bromine} &= (N_{Br \text{ in polymer}} / N_{Br \text{ theoretical}}) \times 100\% = (1.23/1.15) \times 100\% \approx 100\% \\
\text{HB2 polymer:} \\
\text{Area}_{\delta(30.5-31.3)} &= 2N_{B^*} + N_{A^*} = 2.34 \\
\text{Area}_{\delta(55.1-55.9)} &= N_{B^*} = 1.0 \\
N_{A^*} &= 2.34 - 2 \times 1.0 = 0.34 \\
N_{Br \text{ in polymer}} &= N_{A^*} + N_{B^*} = 1.0 + 0.34 = 1.34 \\
\text{Area}_{\delta(62.2-63.7)} &= 2 \\
N_{Br \text{ theoretical}} &= 2.46 \text{ or Area}_{\delta(36.2-37.6)} = N_{Br \text{ theoretical}} = 2.47
\]
\[ N_{Br\,theoretical} = \frac{2.46}{2} = 1.23 \]

Fraction of bromine = \( \frac{N_{Br\,in\,polymer}}{N_{Br\,theoretical}} \times 100\% = \frac{1.34}{1.23} \times 100\% = 109\% \)

The fraction of bromine in the HB1 was determined to be a little bit higher than 100%, which is within the integration error tolerance of NMR measurement which could be about 10%.

Figure 2.1: Representative structure and inverse gated decoupled \(^{13}\)C NMR spectrum of (A) HB1 and (B) HB2 with peak assignments and integration of peaks. Five structural units: focal (F), dendritic (D), terminal (T), and linear (linear vinyl Lv, linear condensation Lc) units; five subunits: unreacted double bond, initiating site from reacted double bond (A*), unreacted initiating site (B*), reacted double bond (a), and reacted initiating site (b).
2.3.2 One-pot synthesis of hyperstar polymers with hydrophobic monomer via seeded emulsion

To demonstrate the concept of one-pot synthesis of hyperstar polymers, the HB1 hyperbranched polymer after microemulsion polymerization \((D_h = 12 \text{ nm})\) in water) was used as a MI without any purification for in-situ polymerization of \(nBA\) monomer in a second step. Addition of 2.7g of \(nBA\) \([nBA]_0:[Br]_0 = 30:1\) into the microemulsion latexes of HB1 formed a seeded emulsion with polymer latexes swollen by the hydrophobic \(nBA\) monomers \((D_h = 45 \text{ nm}, \text{Figure 2.2B})\). The polymerization of \(nBA\) from the hyperbranched MIs was initiated by adding 0.5 equivalent of NaAs in 0.5 mL water and quickly approached 90% \(nBA\) conversion within 20 min (Figure 2.2A). Meanwhile, the \(D_h\) of the latexes was constant during the increase of \(nBA\) conversions, as shown in Figure 2.2B. The THF SEC chromatograms of the purified HS1-PnBA hyperstar polymers in Figure 2.2C show monomodal elution peaks shifting to higher molecular weight direction as the increase of \(nBA\) conversion with no detectable hyperstar-hyperstar coupling signal. Figure 2.2D indicates that the produced hyperstar polymers had linear increase of molecular weight and decreased dispersity versus conversion. These results indicate that the chain extension polymerization of \(nBA\) was isolated in each discrete latex protected by surfactants. The segregated latex space prevented the star-star coupling reactions and produced hyperstar polymers with narrow molecular weight distribution in THF even at 97% \(nBA\) conversion.
Figure 2.2: (A) Conversion of \( nBA \) as a function of time in the synthesis of HS1-P\( nBA \); (B) \( D_h \) evolution of polymer latexes during the synthesis of HS1-PnBA hyperstar polymers determined by DLS; (C) THF SEC chromatograms of the HB1 and HS1-PnBA at various conversions based on linear PMMA standards; (D) Molecular weights and polydispersities (\( M_w/M_n \)) of the purified HS1-PnBA polymers as a function of \( nBA \) conversion.

To demonstrate the importance of emulsified latexes on the structural control of hyperstar polymers, a control experiment of using purified HB1 as MI for normal ATRP of \( nBA \) in bulk was conducted. The polymerization was slower and took 3 hours to reach 90% \( nBA \) conversion (Figure 2.3A). More importantly, the synthesized HS1-PnBA in the bulk polymerization was not soluble in THF since it formed macroscopic gel at 25% conversion (Figure 2.3B). In another experiment,
one-pot polymerization of neutral water-soluble OEGMA\textsubscript{300} from HB1 latexes under the stoichiometric ratio of [OEGMA\textsubscript{300}]:[Br]\textsubscript{0} = 50:1 also reached macroscopic gelation at 28% OEGMA\textsubscript{300} conversion (Figure 2.3C). The result of gelation indicates the lack of steric protection around the HS1-POEGMA hyperstar polymers during the polymerization, which was probably due to the water-soluble characteristic of POEGMA arms. In other words, the formed neutral POEGMA arms radiated out of the surfactant-protected latexes and resulted in a subsequent polymerization in the continuous water phase.

![Figure 2.3](image)

Figure 2.3: (A) Conversion as a function of time in synthesis of HS1-P\textsubscript{n}BA hyperstar polymer via seeded emulsion and bulk routes; (B) Digital picture of the gel of HS1-P\textsubscript{n}BA in bulk synthesis; C) Digital picture of the gel of HS1-POEGMA in one-pot synthesis in aqueous dispersed environment.

2.3.3 One-pot synthesis of hyperstar polymers using zwitterionic monomer under protection of electrostatic repulsion

Instead of using steric segregation in seeded emulsion polymerization to prevent the hyperstar-hyperstar coupling, e.g. in the synthesis of HS1-PnBA, a
second method is to use electrostatic repulsion between polyelectrolyte arms to disfavor coupling reactions and produce hyperstar polymers at high conversion. As a modified amino acid, monomer CysMA shows amphiprotic property by containing both amine and carboxylic acid groups in one molecule. CysMA demonstrates zwitterionic nature\textsuperscript{45} when environmental pH is between its pKa1 = 1.8 and pKa2 = 9.0, determined by titration of 0.2 M CysMA aqueous solution using 1.0 M NaOH solution (Figure 2.4A). When environmental pH is at the midpoint of these two pKa values, the isoelectric point pI = \frac{1}{2}(pKa1 + pKa2) = 5.4 was determined when the monomer CysMA should carry zero net charge.

To demonstrate the importance of environmental pH on the polymerization of CysMA from hyperbranched MI, a one-pot synthesis of HS1-PCysMA hyperstar polymer was carried out under pH = 7.4, where the monomer CysMA and PCysMA polymer were expected to be slightly cationic. At the same time, this mild pH environment would not disturb the polymerization since ATRP has been reported to lose control in either too acidic or too basic environment.\textsuperscript{54-56} Under the stoichiometric ratio of [CysMA]_0:[Br]_0 = 50:1, addition of 0.5 mL of NaAs water solution ([NaAs]_0:[CuBr\textsubscript{2}]_0 = 0.5:1) initiated the polymerization to reach complete CysMA conversion (~99%) within 0.5 hour, evidenced by the disappearance of vinyl group peaks in the \textsuperscript{1}H NMR spectroscopy. Meanwhile, the HS1-PCysMA hyperstar polymers before purification exhibited increased \(D_h\) values in water (pH = 7.4) as the progress of polymerization and ultimately reached \(D_h = 97\) nm at 99% CysMA conversion (Figure 2.4B). This situation was
different from that in the synthesis of HS1-PnBA polymer when constant $D_h$ of latexes was observed throughout the polymerization (Figure 2.2B). After purification by dialysis against DI water and lyophilization, the HS1-PCysMA hyperstar polymer was re-dissolved in pH = 7.4 water and characterized by batch-mode MALLS to determine the weight-average molecular weight $M_w = 7.74 \times 10^6$ using the value of $dn/dc = 0.159 \text{ mL/g}$. Since the absolute molecular weight of HB1 was $3.28 \times 10^5$, the weight fraction of the PCysMA arms in the produced hyperstar polymer was estimated to be around 95%.

The purified hyperstar HS1-PCysMA at preset pH = 0.1 water solution was titrated with 1.0 NaOH solution to determine its apparent pKa1, pKa2 values as 2.0 and 8.9, respectively (Figure 2.4A). These values were different from the CysMA monomer’s probably because of the confined environment of the charged groups in the star polymer, which created higher osmotic pressure inside the star polymer and led to a partial reversal of acid-base ionization behavior. Figure 2.4C indicates significant variation of the zeta $\zeta$ and hydrodynamic sizes $D_h$ of HS1-PCysMA as the environmental pH was elevated from pH = 0.8 to 9.8. Within the range of pH = 0.8 - 2.5, increasing the environmental pH resulted in a decreased $\zeta$ of the HS1-PCysMA from +30 mV to +10 mV and a decreased $D_h$ from 152 nm to 132 nm. Further increasing the pH from pH 2.5 to pH 8.3 created a window with $\zeta$ variation from +10 mV to -10 mV but an almost constant $D_h \sim 110$ nm. This window was largely in agreement to the zwitterionic region of the HS1-PCysMA polymer (2.0 - 8.9), defined by the two pKa values, in which small amounts of net
negative and net positive ions were in dynamic equilibrium within the densely packed star structure.\textsuperscript{58,59} At environmental pH = 4.8, the zeta potential measurement showed a neutral hyperstar polymer with no net charge. Further increasing the pH from 8.5 to 9.8 increased the $D_h$ of HS1-PCysMA polymer from 130 nm to approximately 150 nm as the $\zeta$ changed sharply from -10 mV to -30 mV.

### TABLE 2.1

EFFECT OF ENVIRONMENTAL PH ON THE SYNTHESIS OF HS2-PCYSMA

<table>
<thead>
<tr>
<th>pH\textsuperscript{a}</th>
<th>6.3</th>
<th>7.4</th>
<th>8.2</th>
<th>9.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeta potential \textsuperscript{b} (mV)</td>
<td>-3</td>
<td>-5.5</td>
<td>11</td>
<td>-24</td>
</tr>
<tr>
<td>Product status \textsuperscript{c}</td>
<td>gelled</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
</tbody>
</table>

\textsuperscript{a} pH was tuned by 0.1 M of NaOH or HCl after addition of CysMA monomer before initiation.

\textsuperscript{b} Zeta potential values were read from the titration curve of Figure 2.4C.

\textsuperscript{c} × represents no reaction, ✓ represents successful reaction.
Figure 2.4: (A) Determination of the pKa1, pKa2 and pI of CysMA monomer and HS1-PCysMA hyperstar polymer via titration of 0.2 M aqueous solutions with 1.0 M NaOH solution; (B) Evolution of Dh of HS1-PCysMA at different CysMA conversions in aqueous solution with pH = 7.4, determined by DLS; (C) Dependence of Dh and ζ of HS1-CysMA as a function of pH.
The titration curves in Figure 2.4A and Figure 2.4C confirmed the importance of environmental pH on preventing the hyperstar coupling reactions during the one-pot polymerization of CysMA from the hyperbranched MI. In addition to the successful hyperstar synthesis under environmental pH = 7.4, a series of one-pot polymerization of CysMA using different environmental pH 6.3-9.2 were carried out. The results in Table 2.1 confirmed that the optimal condition for the polymerization of CysMA was pH = 7.4-8.2 when the polyzwitterionic arms carried small amount of charges (-10 mV < ζ < -7 mV), while the environment was not hostile to the polymerization. Within this pH range, the ATRP of CysMA became slower at pH = 8.2 than that at pH = 7.4 (Figure 2.5A), probably due to the stronger electrostatic repulsion between the charged CysMA.
monomer and the HS1-PCysMA hyperstar polymer. In contrast, ATRP of CysMA from the HB1 MI under environmental pH = 6.3, close to the isoelectric point of HS1-PCysMA PI = ½(2.0 + 8.9) = 5.5, resulted in significant hyperstar coupling reactions and gelation at 23% CysMA conversion (Figure 2.5B, Table 2.1).

### TABLE 2.2

#### ONE-POT SYNTHESIS OF HYPERSTAR POLYMERS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conv.</th>
<th>Molecular weight</th>
<th>DLS size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$M_n$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>RI</td>
</tr>
<tr>
<td>HB1</td>
<td>100%</td>
<td>133 ×10$^3$</td>
<td>328 ×10$^3$</td>
</tr>
<tr>
<td>HB2</td>
<td>100%</td>
<td>79 ×10$^3$</td>
<td>299 ×10$^3$</td>
</tr>
<tr>
<td>HS1-PnBA</td>
<td>97%</td>
<td>234 ×10$^3$</td>
<td>1120 ×10$^3$</td>
</tr>
<tr>
<td>HS2-PnBA</td>
<td>98%</td>
<td>199 ×10$^3$</td>
<td>986 ×10$^3$</td>
</tr>
<tr>
<td>HS1-PCysMA</td>
<td>99%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HS2-PCysMA</td>
<td>97%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

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**a** Experimental conditions: 1$^{st}$ step, [inimer]$_0$/[CuBr$_2$]$_0$/[dNbpy]$_0$/[NaAs]$_0$ = 70/1/2/0.5, weight ratio of inimer to Brij98 = 1:4, 1 g of Brij98 in 12 g of water, 65 °C, 2 h; 2$^{nd}$ step, [Br]$_0$/[nBA]$_0$/[CuBr$_2$]$_0$/[dNbpy]$_0$/[NaAs]$_0$ = 1/30/1/2/0.5 for synthesis of HS1-PnBA and HS2-PnBA, [Br]$_0$/[CysMA]$_0$/[CuBr$_2$]$_0$/[dNbpy]$_0$/[NaAs]$_0$ = 1/50/1/2/0.5 for synthesis of HS1-PCysMA and HS2-PCysMA

**b** Monomer conversion determined by $^1$H NMR spectroscopy (entries 1-2, 5-6) and GC (entries 3-4)

**c** Apparent number-average molecular weight and molecular weight distribution determined by THF SEC with RI detector, calibrated with linear PMMA standards. Absolute number-average molecular weight measured by THF SEC with MALLS detector

**d** Volume-average $D_h$ and coefficient of variation (CV) determined by DLS using $dn/dc = 0.084$ mL/g, the $D_h$ of HS1-PCysMA and HS2-PCysMA was measured under pH 7.4 before purification.
2.3.4 Synthesis of degradable hyperstar polymers

In addition to varying the arm composition of the hyperstar polymers in this one-pot synthetic procedure, the use of inimer 2 that contained a disulfide linkage could also produce hyperstar polymers that become liable to degradation under reducing environment. Two hyperstar polymers, HS2-PnBA and HS2-PCysMA, were synthesized using HB2 MIs. After purification, their degradation experiments were carried out at room temperature using DTT as reducing agent and the size evolution of the degraded products was monitored in DLS (Figure 2.6A and Figure 2.6C). For instance, 5 mg of purified HS2-PnBA dissolved in 1 mL of THF showed a monomodal DLS peak with $D_h = 46$ nm at 0 min. After addition of 1 mL DTT (20 mM in THF), the hyperstar polymers started to fall apart and reached the final size with $D_h < 10$ nm in THF at 0.5 hour (Figure 2.6A). Addition of more DTT into the polymer solution did not change the size further. Similar results were observed from the degradation of 5 mg HS2-PCysMA in 1 mL H$_2$O after addition of 1 mL DTT (20 mM) in H$_2$O. The degradability of hyperstar polymers containing disulfide groups in the core provides a method to estimate the number of dangling arms in each hyperstar polymer. For instance, the final degraded product of HS2-PnBA was analyzed by THF SEC and showed a narrow elution peak with $M_n = 2,500$ and $M_w/M_n = 1.41$ based on linear PMMA standards (Figure 2.6B). Since the HB2 hyperbranched MI with $M_{n,MALLS} \approx 299 \times 10^3$ (Table 2.2) contained a theoretical 810 inimer units per polymer molecule and the $M_{n,MALLS}$ of HS2-PnBA was $986 \times 10^3$, the initiation efficiency (IE) of the HB2 MI
during the polymerization of nBA in the seeded emulsion was about 34% \((\text{IE} = (986 \times 10^3/2500)/810 \approx 34\%)\). The incomplete initiation was probably due to the compact environment around the hyperbranched polymer core.

Figure 2.6: (A) Size change before and after the degradation of HS2-PnBA by DTT, determined in THF by DLS; (B) THF SEC curves of the original and final degraded product from HS2-PnBA based on linear PMMA standards; (C) Size change before and after the degradation of HS2-PCysMA by DTT, determined in water by DLS.

2.4 Conclusions

This research presents the synthesis of hyperstar polymers using a one-pot two-batch process. After ATRP of inimer in an oil-in-water microemulsion to produce a hyperbranched MI with well-defined structure, a second batch of monovinyl monomer was added into the polymer latexes without breaking the microemulsion for subsequent growth of the radiating arms. Two types of monomers with different functional groups and polarities were applied in this one-pot procedure to demonstrate the efficient synthesis of hyperstar polymers.
with no detectable hyperstar-hyperstar coupling reactions. The hydrophobic nBA monomer after addition to the microemulsion diffused into the latex and swelled the hyperbranched polymers forming a seeded emulsion, which protected the growth of PnBA arms to produce structurally defined hyperstar polymers with high monomer conversion. The polymerization of zwitterionic CysMA monomer grew polyelectrolyte arms from the hyperbranched MI, which stabilized the hyperstar polymers in aqueous phase and inhibited the hyperstar-hyperstar coupling because of electrostatic repulsion. When inimer containing disulfide linker group was used, the hyperstar polymers exhibited rapid degradation in reducing environment and generated linear polymers as the degraded product.

2.5 Acknowledgments

I would like to thank Dr. Ke Min for helping me to learn the microemulsion techniques. I would also want to acknowledge Robert W. Graff for helping me in the interpretation of inverse-gated decoupled $^{13}$C NMR data for DB determination of hyperbranched polymers.

2.6 References


CHAPTER 3:
SYNTHESIS OF HYPERBRANCHED POLYMERS WITH HIGH MOLECULAR WEIGHT IN THE
HOMOPOLYMERIZATION OF POLYMERIZABLE TRITHIOCARBONATE TRANSFER AGENT
WITHOUT THERMAL INITIATOR

3.1 Introduction

In the past few decades, both dendrimers and hyperbranched polymers are popularly studied and proposed as promising types of nanostructured polymers due to their attractive structural features, including compact three-dimensional structures, cavernous interior and large number of peripheral groups. Unlike dendrimers, hyperbranched polymers can be easily synthesized in a one-pot polymerization following several different techniques: polymerization of \( \text{AB}_m \) (\( m \geq 2 \)) monomers (with or without the use of multifunctional \( \text{B}_f \) core),\(^{9-28}\) copolymerization of \( \text{A}_n \) and \( \text{B}_m \) monomers (e.g., \( \text{A}_2 + \text{B}_3 \)),\(^{29-32}\) polymerization of divinyl or multivinyl crosslinkers (in the presence or absence of monovinyl monomers),\(^{33-41}\) and SCVP of polymerizable initiators, often known as \textit{inimers}. The last technique requires the use of controlled polymerization
methods, such as CRP,\textsuperscript{42-52} living ionic polymerization,\textsuperscript{53-57} ring opening metathesis polymerization (ROMP),\textsuperscript{58} and group transfer polymerization.\textsuperscript{59}

Among the various CRP methods, ATRP\textsuperscript{43,45,46,60-63} and NMP\textsuperscript{42,47,64-66} have been first applied for the homopolymerization of inimers or copolymerization with various functional monovinyl monomers to produce hyperbranched and branched polymers. It is important to note that the use of large excess of monovinyl monomers in the copolymerization with inimers is expected to decrease the degree of branching (DB) of the polymers, and produce branched (instead of hyperbranched) polymers. In contrast, less reports have been published on the RAFT polymerization of polymerizable chain-transfer agents (i.e., transmers), and even fewer studies have investigated the homopolymerization of transmers to produce high-DB hyperbranched polymers.\textsuperscript{48-50,67-84}

Different from AB* inimers that could generate propagating radicals under proper initiation conditions, the transmers in the RAFT polymerization typically requires external radical source, such as 2,2'-azobisisobutylnitrile (AIBN) for initiation and polymerization.\textsuperscript{52} The presence of primary radicals throughout the polymerization system has profound effect on the radical-vinyl reactions and radical-radical termination reactions, which have significant effect on the structures and the molecular weights of the hyperbranched polymers.\textsuperscript{84} A thorough literature research within the best of our knowledge indicates that RAFT homopolymerization of transmers when using thermal initiators as radical sources could only produce hyperbranched polymers with low molecular weight. Several groups have reported results for RAFT homopolymerization of transmers, including Zhao group with the highest molecular weight as $M_n = 24,700$,\textsuperscript{71}
Sumerlin group with $M_n = 8,740^{70}$ and Poly group with $M_n \sim 1,000^{84}$. Many groups simply used more monovinyl monomers, i.e., high ratios of $[\text{monomer}]_0/[\text{transmer}]_0$, to increase the molecular weights.$^{48-50,67-84}$ On the other hand, Ishizu and Tanaka reported the photo-polymerization of dithiocarbamate-containing styrenyl monomer without using thermal initiator and produced hyperbranched polymers with molecular weight above 100,000,$^{85,86}$ although no detailed polymerization kinetics and comparison to thermal RAFT system were studied.

With the intention to increase the molecular weights of hyperbranched polymers in the homopolymerization of transmers, we in this contribution systematically studied the evolution of the polymer molecular weights and the polymer structures when thermal initiator was used as the radical source. Based on the results, a new initiation system was applied to effectively produce high-molecular-weight hyperbranched polymers, including the concurrent RAFT/ATRP of transmers using copper catalyst and the ATRP inimers.
Scheme 3.1. Schematic illustration of homopolymerization of transer (1) using (A) RAFT with PEG-azo thermal initiator and (B) concurrent ATRP/RAFT without thermal initiator.

3.2 Experimental

3.2.1 Materials

4,4'-Azobis(4-cyanovaleric acid) (Alfa Aesar, 98%), carbon disulfide (Alfa Aesar, 98%), butanethiol (Alfa Aesar, 98%), 2-bromoisobutyric acid (Alfa Aesar, 98%), acetone (BDH chemicals, 98%), 2-hydroxyethyl methacrylate (HEMA, Sigma-Aldrich, 98%), glycidyl methacrylate (GMA, Sigma-Aldrich, 97%), α-bromoisobutyryl bromide (Sigma-Aldrich, 98%), pyridine (Sigma-Aldrich, 99.8%), 4,4'-dinonyl-2,2'-dipyridyl (dNbp, Sigma-Aldrich, ≥99%), 4-3-(3-dimethylaminopropyl)-1-ethyl-carbodiimide hydrochloride (EDC-HCl, Chem-Impex), 4-(dimethylamino) pyridine (DMAP, Sigma-Aldrich, 99%), 1,1'-
azobis(cyclohexanecarbonitrile (V-40, Aldrich 98%), poly(ethylene glycol) methyl ether (MeO-PEG-OH, \( M_n = 550 \), Sigma-Aldrich, 99%), dichloromethane (DCM, Sigma-Aldrich, >99.5%), sodium hydroxide (Sigma-Aldrich, 99.8%) were used as received. CuBr (98%, Aldrich) was purified using a modified literature procedure.\(^{87}\) PEG-azo thermal initiator was synthesized by esterification reaction of azo initiator 4,4′-azobis(4-cyanovaleric acid and PEG-OH. 2-(2-Bromoiso-butylryloxy) ethyl methacrylate (inimer 1),\(^{88}\) and transmer 2-((2-(((butylthio)carbonothioyl)thio)-2-methylpropanoyl)oxy)ethyl methacrylate\(^{89}\) were synthesized according to reported methods.

3.2.2 Characterizations

Nuclear magnetic resonance (NMR) spectroscopy was carried out on a Bruker DM × 500MHz spectrometer operated in the Fourier transform mode. After filtration through 0.45 µm PTFE filter, the polymer samples were separated by size exclusion chromatography (SEC) with tetrahydrofuran (THF) as mobile phase. The THF SEC was equipped with Polymer Standards Services (PSS) columns (guard, \( 10^5 \), \( 10^3 \), and \( 10^2 \) Å SDV columns) at 35 °C with THF flow rate = 1.00 mL/min, a differential refractive index (RI) detector (Wyatt Technology, Optilab T-rEX) using PSS WinGPC 7.5 software. The apparent molecular weights were calculated based on linear poly(methyl methacrylate) (PMMA) standards. The detectors employed to measure the absolute molecular weights of hyperbranched polymers in THF SEC were the RI detector and a multi-angle laser light scattering (MALLS) detector (Wyatt Technology, DAWN HELEOS II) with the light wavelength at 658 nm. Absolute molecular weights were determined using 1) Astra
software from Wyatt Technology with the $dn/dc = 0.11 \text{ mL/g}$, determined via an off-line measurement of five polymer solutions with different concentrations ($0.25 \text{ mg mL}^{-1}$, $0.5 \text{ mg mL}^{-1}$, $1.0 \text{ mg mL}^{-1}$, $3.0 \text{ mg mL}^{-1}$, $6.0 \text{ mg mL}^{-1}$) for high-molecular-weight polymers; and $^{1}$H NMR based on the equation: $M_{n,NMR}$ molecular weight = (molar mass of transmer × number of repeating ethylene linker)/(number of PEG focal group + number of vinyl focal groups).

3.2.3 Synthetic procedures

3.2.3.1 Synthesis of transmer 1, trithiocarbonate chain transfer agent (TTC-CTA) and initiators

2-(Butylthio-carbonothioylthio)-2-methylpropanoic acid (Compound 1) was synthesized as followed: A 250-mL three-neck round-bottom flask (fitted with septum and reflux condenser with $N_2$ bubbler was charged with 60 mL of acetone followed by the addition of a solution of sodium hydroxide (2.64g, 66 mmol) in 45 mL of acetone/water mixture. The temperature of the mixture was maintained between 5 and 15 °C. 1-Butane thiol (5.95g, 66 mmol) was added over 10 min to the round-bottom flask and the mixture was stirred for 45 min. To this white slurry, carbon disulfide (5.0g, 66 mmol) was added over 15 min, and it was stirred for an additional period of 1 hour, before warmed up to room temperature and stirred for a further period of 1 hour. 2-Bromo-2-methyl propionic acid (11.0g, 66 mmol) was then slowly added and the mixture was stirred for 24 hour. The reaction mixture was then poured into water, which was followed by extraction with ethyl acetate. The combined extracts were dried
with anhydrous MgSO$_4$ and filtered. The solvent was removed using a rotary evaporator. The crude product was recrystallized three times with hexanes to provide pure Compound 1 as a yellow color solid with yield: 70%. $^1$H NMR (in CDCl$_3$, δ, ppm): 0.83-0.88 (3H, $H_3$CCH$_2$CH$_2$CH$_2$), 1.32-1.38 (2H, CH$_3$CH$_2$CH$_2$CH$_2$), 1.53-1.58 (2H, CH$_3$CH$_2$CH$_2$CH$_2$), 1.61-1.65 (6H, SC(CH$_3$)$_2$CH$_2$COO), 3.20-3.24(2H, CH$_3$CH$_2$CH$_2$CH$_2$).

Transmer 1 was then synthesized as followed: to a 250 mL round-bottom flask were added sequentially with compound 1 (10.8 g, 40 mmol), HEMA (5.72 g, 44 mmol), EDC·HCl (17.4 g, 80 mmol), dry DCM (120 mL) and DMAP (2.16g, 17.7 mmol). The reaction mixture was allowed to be stirred at room temperature overnight before washed with water (2×50 mL) and brine (2×50 mL), and dried over MgSO$_4$. The solvent was evaporated, and the remaining residual was purified by silica gel chromatography (hexanes/diethyl ether, 4:1 v/v) to give 12.4 g light yellow liquid of the targeted monomer (82% yield). $^1$H NMR (in CDCl$_3$, δ, ppm): 0.81-0.88 (3H, $H_3$CCH$_2$CH$_2$CH$_2$), 1.32-1.28 (2H, CH$_3$CH$_2$CH$_2$CH$_2$), 1.52-1.58 (2H, CH$_3$CH$_2$CH$_2$CH$_2$), 1.61-1.65 (6H, SC(CH$_3$)$_2$CH$_2$COO), 1.85-1.87(3H, CH$_3$C=CH$_2$), 3.15-3.21(2H, CH$_3$CH$_2$CH$_2$CH$_2$), 4.26-4.30 (4H, OCH$_2$CH$_2$O), 5.4-6.2(2H, CH$_2$=CCOO).

The TTC-CTA was synthesized by using similar procedure as that of transmer 1 except that the esterification was carried out with methanol (92% yield). $^1$H NMR (in CDCl$_3$, δ, ppm): 0.81-0.88 (3H, $H_3$CCH$_2$CH$_2$CH$_2$), 1.32-1.28 (2H, CH$_3$CH$_2$CH$_2$CH$_2$), 1.52-1.58 (2H, CH$_3$CH$_2$CH$_2$CH$_2$), 1.61-1.65 (6H, SC(CH$_3$)$_2$CH$_2$COO), 1.85-1.87(3H, CH$_3$C=CH$_2$), 3.15-3.21(2H, CH$_3$CH$_2$CH$_2$CH$_2$), 3.61-3.62 (3H, CH$_3$OC=O).
PEG-azo initiator was synthesized as followed: To a 50 mL round-bottom flask were added sequentially with 4,4'-azobis(4-cyanovaleric acid) (1.4 g, 5 mmol), PEG-OH (5.5 g, 10 mmol), EDC·HCl (1.9 g, 10 mmol), dry DCM (120 mL) and DMAP (0.2 g, 1.7 mmol). The reaction mixture was allowed to be stirred at room temperature overnight before washed with water (2×20 mL), brine (50 mL), and dried over MgSO$_4$. The crude product in DCM was then passed through a basic aluminum column to remove the brownish color before dropwise addition into cold diethyl ether to precipitate out the PEO-azo initiator. Meanwhile, the unreacted PEG-OH 550 was still soluble in the cold diethyl ether due to different solubility. The precipitates were then collected and redissolved in DCM for two more rounds of precipitation in cold diethyl ether before drying the final product, PEG-azo initiator, under vacuum at room temperature for 2 hours (75% yields). $^1$H NMR (in CDCl$_3$, δ, ppm): 1.71-1.73 (6H, 2×C$_3$H$_3$CCN), 2.33-2.61 (8H, 2×C$_2$H$_2$COO), 3.52-3.55 (6H, 2×C$_3$HOCH$_2$CH$_2$O), 3.72-3.93 (~2×45H, OCH$_2$CH$_2$O), 4.52-4.61 (4H, 2×COOCH$_2$CH$_2$).

3.2.3.2 Synthesis of 2-(2-bromoisobutyryloxy) ethyl methacrylate (BIEM inimer)$^{91}$

A 100 mL round bottom flask was loaded with a magnetic stir bar, HEMA (12.13 mL, 0.10 mol), pyridine (8.60 mL, 0.11 mol), and 70 mL DCM, before being cooled to 0°C in an ice bath. 2-Bromoisobutyryl bromide (12.36 mL, 0.10 mol) was dissolved in 15 mL DCM and added to the reaction mixture via addition funnel over 45 min. The reaction was kept cold for an additional 45 min before being warmed up to room temperature for an additional 3 hours. After the reaction, the solvent was removed under reduced
pressure before the product was purified on a silica column (4:1 hexanes: ethyl acetate), obtaining 25.68 g clear oil (92% yield). $^{1}$H NMR (in CDCl$_3$, δ, ppm): 6.07 (1H, CH$_2$=C(CH$_3$)), 5.52 (1H, CH$_2$=C( CH$_3$)), 4.35 (4H, OCH$_2$CH$_2$O), 1.88 (3H, CH$_2$=C(CH$_3$)$_3$), and 1.86 (6H, C(CH$_3$)$_3$Br).
Figure 3.1: $^1$H NMR spectra of A) compound 1; B) transmer 1; C) TTC-CTA; D) PEG-azo initiator, and E) BIEM inimer.
3.2.3.3 Polymerization of transmer with different initiators

All experimental procedures for synthesis of hyperbranched polymers in solution were similar with slight difference when using different initiators.

Polymerization of transmer initiated by azo initiator with $[\text{transmer } 1]_0/[\text{PEG-azo}]_0 = 50/1$. A clean and dry 10 ml Schlenk flask was charged with transmer 1 (1 g, 2.75 mmol), PEG-azo initiator (76 mg, 0.055 mmol) and 3 mL toluene, the flask was deoxygenated by five freeze-pump-thaw cycles before it was immersed in an oil bath at 65 °C to start the polymerization.

The polymerization of transmer with $[\text{transmer } 1]_0/[\text{CuBr}]_0/[\text{dNbpy}]_0 = 50/1/1/2$. A clean and dry 10 ml Schlenk flask was charged with transmer 1 (1 g, 2.75 mmol), dNbpy (44 mg, 0.11 mmol) and 3 mL toluene, the flask was deoxygenated by five freeze-pump-thaw cycles. During the final cycle, the flask was filled with nitrogen before CuBr (8 mg, 0.055 mmol) was quickly added to the frozen mixture. The flask was sealed with a glass stopper then evacuated and back-filled with nitrogen five times before it was immersed in an oil bath at 65 °C to start the polymerization.

The polymerization of transmer with $[\text{transmer}]_0/[\text{BIEM}]_0/[\text{CuBr}]_0/[\text{dNbpy}]_0 = 50/1/1/2$. A clean and dry 10 ml Schlenk flask was charged with transmer 1 (1 g, 2.75 mmol), BIEM (15.3 mg, 0.055 mmol), dNbpy (44 mg, 0.11 mmol) and 3 mL toluene; the flask was deoxygenated by five freeze-pump-thaw cycles. During the final cycle, the flask was filled with nitrogen before CuBr (8 mg, 0.055 mmol) was quickly added to the frozen mixture. The flask was sealed with a glass stopper then evacuated and back-filled with
nitrogen five times before it was immersed in an oil bath at 65 °C to start the polymerization.

During the polymerizations, samples were withdrawn at timed intervals for the analysis of vinyl group conversion and polymer molecular weight via $^1$H NMR and THF SEC, respectively. After expected reaction conversion, the reactions were stopped by exposure to air and dilution with THF. The solution was filtered through a column filled with neutral alumina and the final polymer was obtained after precipitation into methanol and drying under vacuum.

3.2.3.4 Purification of polymer samples

To completely remove the unreacted transmers and free PEG chains, each polymer sample was dissolved in DCM and precipitated into methanol for four times by adding methanol into the DCM solution. For instance, the hyperbranched polymer sample collected from the reaction ([transmer 1]$_0$/[PEG-azo]$_0$ = 50/1, toluene as solvent, 65°C, [transmer 1]$_0$ = 0.75 mol L$^{-1}$) at 36 hours was purified for four times. The product after each purification step was characterized using $^1$H NMR spectroscopy to monitor the peak intensities of PEG chains and vinyl groups (Figure 3.2). The results show that the intensities of these peaks stopped changing after three cycles of purification, ensuring that there was no unreacted transmers and free PEG chains in the final purified samples. Similar purification procedures were applied to all other samples before careful NMR characterization.
3.3 Results and Discussion

3.3.1 Polymerization of transmer with azo-thermal initiator

Within our best knowledge, traditional RAFT homopolymerization of transmers when using thermal initiator as radical source failed to produce high-molecular-weight hyperbranched polymers. To understand the reason and track the evolution of polymer structure in NMR spectroscopy, a PEG-labelled thermal azo initiator (termed as PEG-azo) was synthesized via esterification between 4,4′-azobis(4-cyanovarlic acid) and PEG methyl ether (MeO-PEG-OH, $M_n = 550$). The RAFT homopolymerization of transmer 1
was conducted with \([\text{transmer } 1]_0/[\text{PEG-azo}]_0 = 50/1\) with toluene as solvent at 65°C, 
\([\text{transmer } 1]_0 = 0.75 \text{ mol L}^{-1}\). Samples were taken at timed intervals for \(^1\text{H} \text{NMR}\) and THF SEC measurements of vinyl conversions and polymer molecular weights, respectively. At 
48 hours, the polymerization reached over 98% vinyl conversion (Figure 3.3A) and the 
molecular weight stopped increasing at \(M_n,\text{RI} = 5,600\) (Figure 3.3B and Figure 3.3C), 
determined by THF SEC based on linear poly(methyl methacrylate) (PMMA) standards. 
As comparison, the absolute molecular weights of the hyperbranched polymers 
determined by MALLS detector (measured \(dn/dc = 0.11 \text{ mL/g}\)) became measurable only 
at high conversions. The values of \(M_n,\text{MALLS}\) were higher than the \(M_n,\text{RI}\), confirming the 
compact structure of the hyperbranched polymers (Table 3.1, entry 3).

The series of polymer samples at various conversions, including the final 
polymer, were thoroughly purified, i.e., precipitation into methanol for four times to 
completely remove the unreacted transmer and unincorporated PEG. Figure 3.4A shows 
the stacked \(^1\text{H} \text{NMR}\) spectra of the purified polymers, identifying the evolution of four 
key moieties in the polymer structure: the trithiocarbonate (TTC) group, the focal vinyl 
(V_{foc}) group, the dangling PEG group and the vinyl group from disproportionation 
reaction (V_{disp}). It should be noted that the complicated structure of hyperbranched 
polymers has posted a great challenge to obtain accurate integration of NMR peaks. 
Three independent NMR measurements of each sample were taken to average the 
integration areas with error bar included. By using the ethylene linker in each transmer 
unit as internal reference, the molar ratios of these four groups to the \(\text{C}_2\text{H}_4\) linker were 
recorded as the function of transmer conversion (Figure 3.4B). The molar fraction of the
$V_{\text{foc}}$ group, the peak at $\delta = 6.12$ ppm, decreased rapidly with conversion and ultimately became undetectable. Since the molecular weight of the final hyperbranched polymer was merely $M_{n,\text{MALLS}} = 10,100$ (DP $\sim$ 30), the trend of $V_{\text{foc}}$ vs conversion indicates that many focal vinyl groups were consumed but helped little to the increase of polymer molecular weights, probably through the intramolecular cyclization reactions. Meanwhile, the molar ratio of TTC group decreased with conversion, confirming the occurrence of radical termination reactions. By the end of polymerization, about 4-5% of TTC groups were lost via several possible termination reaction pathways, including coupling and disproportionation reactions with either another propagating radical or a PEG-based primary radical (Scheme 3.1A). Among these several pathways, the coupling termination with PEG primary radicals was confirmed by the increased molar fraction of PEG, the peak at $\delta = 3.64$ ppm, with conversion (Figure 3.4B). On the other hand, the peak at $\delta = 6.20-6.25$ ppm, the protons in $V_{\text{disp}}$ groups produced in the disproportionation reaction, showed increased fraction with conversion. If we take the knowledge that the ratio of disproportionation/combination in methacrylate radicals was about 3/1 to 4/1,\textsuperscript{92-95} the loss of 4% of TTC by the end of polymerization indicates ca. 1.5% $V_{\text{disp}}$ was generated in total. Since the detected amount of $V_{\text{disp}}$ at the end of polymerization was less than 1%, it is speculated that some of the $V_{\text{disp}}$ groups could be consumed in the polymerization via reaction with radicals, although its contribution to the increase of polymer molecular weight was very limited (Figure 3.3B). Furthermore, the marginal increase of molecular weight also confirmed that the coupling termination
reaction between two propagating radicals was either rare or only limited within intramolecular reaction.

Radical termination reactions played an important role in the RAFT homopolymerization of transmers to incorporate $V_{disp}$ groups and primary radical fragments into the polymer structure, although its effect on the increase of molecular weight was marginal. Since the decomposition half time ($t_{1/2}$) of the used PEG-azo thermal initiator at 65°C is around $t_{1/2} = 10$ hours, 97% of the initially added PEG-azo had decomposed after 48 hours (5 $t_{1/2}$ cycles). The lack of primary radicals in the RAFT system stopped the polymerization, producing a hyperbranched polymer with $M_{n,MALLS} = 10,100$. 
Figure 3.3: A) Vinyl conversion as a function of polymerization time; B) overlaid SEC chromatograms of hyperbranched polymers during the polymerization; C) dependence of molecular weights as a function of vinyl conversion in the RAFT homopolymerization with [transmer 1]₀/[PEG-azo]₀ = 50/1, 65°C, [transmer 1]₀ = 0.75 mol L⁻¹. \(M_{n,\text{RI}}\) (based on linear PMMA standards) and \(M_{n,\text{MALLS}}\) were determined from THF SEC coupled with RI and MALLS detectors.
Figure 3.4: A) Overlaid $^1$H NMR spectra of purified hyperbranched polymers and B) molar ratio of each structural moieties in the polymers as a function of vinyl conversion, the RAFT homopolymerization with [transmer 1]$_0$/[PEG-azo]$_0 = 50/1, 65^\circ$C, [transmer 1]$_0 = 0.75$ mol L$^{-1}$. 
To further increase the polymer molecular weight, several experimental parameters were varied to increase the radical concentration or extend its presence time in the RAFT system. The first attempt was to adjust the initial molar ratios of transmer to azo initiator and the results (Table 3.1, entries 1-6) show a mixed influence on the molecular weights. More PEG-azo initiator caused faster and complete consumption of vinyl groups but also introduced more PEG fragments into the polymer. Within the investigated feed ratios of $[\text{transmer 1}]_0/[\text{PEG-azo}]_0 = 10/1, 25/1, 50/1, 100/1, 500/1$ and $2000/1$, the highest molecular weight produced was $M_{n,RI} = 5,600$ when $[\text{transmer 1}]_0/[\text{PEG-azo}]_0 = 50/1$ (Figure 3.5A). High ratios of $[\text{transmer 1}]_0/[\text{PEG-azo}]_0 = 500/1$ and $2000/1$ generated low radical concentration and resulted in incomplete vinyl conversions at the end of polymerization as 78% and 63%, respectively (Figure 3.5B). Meanwhile, the polymerizations using lower ratios of $[\text{transmer 1}]_0/[\text{PEG-azo}]_0 = 25/1$ and $10/1$ reached complete consumption of vinyl groups, but produced more hyperbranched polymers with more PEG groups (Figure 3.5B) and lower molecular weight.
Figure 3.5: A) SEC curves of hyperbranched polymers synthesized with various azo initiators in different amounts, addition modes, and polymerization temperatures; B) $^1$H NMR spectra of purified hyperbranched polymers synthesized by RAFT homopolymerization of transmer 1 using various azo initiators.
### TABLE 3.1

HYPERBRANCHED POLYMERS PRODUCED BY HOMOPOLYMERIZATION OF TRANSFER 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiation</th>
<th>Feed ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Temp./&lt;sup&gt;b&lt;/sup&gt;ºC</th>
<th>( M_n,RI^b )</th>
<th>( M_w/M_n^b ) (RI)</th>
<th>( M_n,MALLS^c )</th>
<th>( M_w/M_n^c ) (MALLS)</th>
<th>DB&lt;sup&gt;d&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>1</td>
<td>PEG-azo</td>
<td>10/1</td>
<td>65</td>
<td>4,700</td>
<td>1.37</td>
<td>9,300</td>
<td>1.19</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>PEG-azo</td>
<td>25/1</td>
<td>65</td>
<td>5,100</td>
<td>1.47</td>
<td>9,500</td>
<td>1.18</td>
<td>-</td>
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<td>PEG-azo</td>
<td>50/1</td>
<td>65</td>
<td>5,600</td>
<td>1.35</td>
<td>10,100</td>
<td>1.18</td>
<td>0.32</td>
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<td>PEG-azo</td>
<td>100/1</td>
<td>65</td>
<td>5,200</td>
<td>1.48</td>
<td>9,700</td>
<td>1.17</td>
<td>-</td>
</tr>
<tr>
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<td>PEG-azo</td>
<td>500/1</td>
<td>65</td>
<td>3,900</td>
<td>1.43</td>
<td>7,200</td>
<td>1.30</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>PEG-azo</td>
<td>2000/1</td>
<td>65</td>
<td>3,800</td>
<td>1.39</td>
<td>6,200</td>
<td>1.49</td>
<td>-</td>
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<td>7</td>
<td>PEG-azo</td>
<td>50/1</td>
<td>50</td>
<td>5,700</td>
<td>1.39</td>
<td>11,700</td>
<td>1.26</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>PEG-azo</td>
<td>50/(1×5)</td>
<td>65</td>
<td>6,200</td>
<td>1.28</td>
<td>14,300</td>
<td>1.28</td>
<td>-</td>
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<tr>
<td>9</td>
<td>V-40</td>
<td>50/1</td>
<td>65</td>
<td>5,900</td>
<td>1.40</td>
<td>12,400</td>
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<td>-</td>
</tr>
<tr>
<td>10</td>
<td>CuBr/(dNbpy)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>10/1</td>
<td>65</td>
<td>32,500</td>
<td>18.60</td>
<td>327,800</td>
<td>5.29</td>
<td>-</td>
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<tr>
<td>11</td>
<td>CuBr/(dNbpy)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>25/1</td>
<td>65</td>
<td>41,300</td>
<td>21.23</td>
<td>389,300</td>
<td>5.65</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>CuBr/(dNbpy)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>50/1</td>
<td>65</td>
<td>48,100</td>
<td>26.93</td>
<td>434,400</td>
<td>5.17</td>
<td>0.30</td>
</tr>
<tr>
<td>13</td>
<td>CuBr/(dNbpy)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>200/1</td>
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<td>50,700</td>
<td>23.57</td>
<td>478,900</td>
<td>5.23</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>CuBr/(dNbpy)&lt;sub&gt;2&lt;/sub&gt; + BIEM</td>
<td>50/1</td>
<td>65</td>
<td>51,900</td>
<td>38.23</td>
<td>635,500</td>
<td>5.68</td>
<td>0.31</td>
</tr>
</tbody>
</table>

<sup>a</sup>[Transmer 1]<sub>0</sub>:[PEG-azo]<sub>0</sub> for entries 1-7, [Transmer 1]<sub>0</sub>:[PEG-azo]<sub>0</sub> = 50:1+1+1+1+1 for entry 8, in which the PEG-azo initiator was added in 5 batches with interval of 24 h; [Transmer 1]<sub>0</sub>:[V-40]<sub>0</sub> for entry 9, [Transmer 1]<sub>0</sub>:[CuBr/(dNbpy)<sub>2</sub>]<sub>0</sub> for entries 10-14, [BIEM]<sub>0</sub> = [CuBr/(dNbpy)<sub>2</sub>]<sub>0</sub> in entry 14. All experiments were conducted at fixed concentration [transmer 1]<sub>0</sub> = 0.75 mol L<sup>-1</sup>.  

<sup>b</sup>Apparent number-average molecular weight and molecular weight distribution measured by THF SEC with RI detector, based on linear PMMA standards.  

<sup>c</sup>Number-average molecular weight and molecular weight distribution measured by THF SEC with MALLS detector (dn/dc=0.11 mL/g).  

<sup>d</sup>Degree of branching (DB) of the hyperbranched polymers, determined by inverse gated decoupled quantitative<sup>13</sup>C NMR spectroscopy.

In addition to varying the molar ratio of transmer 1 to PEG-azo initiator, other methods were also tried, including 1) the decrease of polymerization temperature from 65°C to 50°C to extend the presence time of primary radicals (Table 3.1, entry 7), 2) multiple-batch addition of PEG-azo into the polymerization (Table 3.1, entry 8) and 3)
the use of initiator 1,1'-azobis(cyclohexanecarbonitrile) (V-40) that has a longer half decomposition time at 65°C \( (k_d = 6.7 \times 10^{-7} \text{ s}^{-1}, t_{1/2} \sim 300 \text{ h at } 65^\circ\text{C}) \) \(^{97}\) Table 3.1, entry 9). All three strategies worked in the polymerizations but only marginally improved the molecular weight of the hyperbranched polymers to \( M_{n,RI} = 5,700 – 6,200 \) (Figure 3.5A).

### 3.3.2 Polymerization of transmer with initiation of copper catalyst to produce high-molecular-weight hyperbranched polymers

All efforts by using thermal initiators as radical sources achieved limited success to produce high-molecular-weight hyperbranched polymers. As a new effort in the current study, we decided to use ATRP copper catalyst for activation of the alkyl TTC and provided radicals for the RAFT polymerization with no use of thermal initiators. It has been reported that dithioester and dithiocarbamate chain transfer agents could be effectively activated using CuBr/ligand to conduct a concurrent ATRP/RAFT.\(^{98-100}\) However, the activation of TTC-based chain transfer agent using CuBr/ligand activator has not been reported. The TTC-based transmer 1, was first tested for homopolymerization using 2 mol% of CuBr at \([\text{transmer 1}]_0/[\text{CuBr(dNbpy)}_2]_0 = 50/1\) at 65°C. During the polymerization, the SEC traces of hyperbranched polymers indicated a slow and steady increase of molecular weights over a 2 week reaction time (Figure 3.6A and Figure 3.6C). The molecular weight increased slowly before 96% vinyl conversion followed by an eruptive increase of molecular weight and dispersity at very late stage (Figure 3.6B). Hyperbranched polymers at 350 hours with vinyl conversion \( \sim 99.9\%\) represented the last sample that could be separated by the SEC columns (Figure 3.6C),
which showed an absolute molecular weight $M_{n, MALLS} = 434.4k$ (Table 3.1, entry 12). The polymerization continued after 350 hours although the system became too viscous to be magnetically stirred.

Figure 3.6: A) Vinyl conversions as a function of polymerization time; B) Molecular weight ($M_{n, RI}$) and dispersity ($M_w / M_n$) of hyperbranched polymers in the polymerizations with for 
$[\text{transmer 1}]_0/[\text{CuBr(dNbpy)}_2]_0 = 50/1$ and $[\text{transmer 1}]_0/[\text{BIEM}]_0/[\text{CuBr(dNbpy)}_2]_0 = 50/1/1$ at 65°C, [transmer 1]$_0 = 0.75$ mol L$^{-1}$; C) overlaid SEC curves; D) molar ratio of each structural moieties in the hyperbranched polymers produced from $[\text{transmer 1}]_0/[\text{CuBr(dNbpy)}_2]_0 = 50/1$ at 65°C.
After thorough purification, a series of polymer samples at different conversions were characterized in $^1$H NMR spectroscopy (Figure 3.7). The molar ratios of TTC group, $V_{foc}$ group and $V_{disp}$ group versus the internal reference $C_2H_4$ group were monitored as function of transmer conversions. By the end of polymerization, the molecular weight reached $M_{n,MALLS} = 434.4K$, much higher than that in the PEG-azo initiated system. It was noticed that ca. 18% of TTC groups were lost from the hyperbranched polymers, which was higher than the 2 mol % of CuBr catalyst initially added (Figure 3.6D). A control experiment by mixing a structurally similar TTC chain transfer agent, TTC-CTA with 2 mol % of CuBr(dNbp) under similar conditions confirmed that extended heating at 65 °C caused about 23.4% loss of TTC groups from the isobutyryl moieties after 100 h (Figure 3.8), maybe due to some Cu-catalyzed TTC transformation reactions. Meanwhile, the conversion-dependent evolutions of $V_{foc}$ and $V_{disp}$ groups in Figure 3.6D were similar as those in Figure 3.3B, suggesting their similar reaction behaviors. Therefore, the significant increase of molecular weight in the concurrent ATRP/RAFT system was due to the lack of primary radicals. All termination reactions were between propagating radicals, and the intermolecular coupling termination reactions made major contribution to the increase of molecular weight.
Figure 3.7: Overlaid $^1$H NMR spectra of purified hyperbranched polymers produced from concurrent ATRP/RAFT homopolymerization of [transmer 1]/[CuBr(dNbpy)$_2$] = 50/1 at 65°C, [transmer 1]$_0$ = 0.75 mol L$^{-1}$.

Figure 3.8: (A) Stacked $^1$H NMR spectra and (B) evolution of TTC loss as a function of reaction time in the control experiment: [TTC-CTA]/[Cu(dNbpy)$_2$]$_0$ = 50/1 in toluene at 65 °C, [TTC-CTA]$_0$ = 0.75 mol L$^{-1}$. 

Figure 3.8: (A) Stacked $^1$H NMR spectra and (B) evolution of TTC loss as a function of reaction time in the control experiment: [TTC-CTA]/[Cu(dNbpy)$_2$]$_0$ = 50/1 in toluene at 65 °C, [TTC-CTA]$_0$ = 0.75 mol L$^{-1}$. 

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3.3.3 Polymerization of transmer with initiation of ATRP inimer and copper catalyst to produce high-molecular-weight hyperbranched polymers

It was noticed that the activation of TTC groups using CuBr/(dNbpy)$_2$ catalyst was slow and the low radical concentration explained the need of two weeks to reach very high molecular weight. Further varying the initial feed ratio of [transmer 1]$_0$/[CuBr(dNbpy)$_2$]$_0$ from 10:1 to 200:1, at fixed concentration of [transmer 1]$_0$ = 0.75 mol L$^{-1}$, could adjusted the polymerization rate although all the polymerizations required days to reach complete (>99.8%) conversion (Figure 3.9A and Figure 3.9B). A control RAFT polymerization of MMA using a structurally similar TTC chain transfer agent, 2-(((butylthio)carbonothioyl)thio)-2-methylpropanoate (TTC-CTA) was set up in toluene under 65°C with [MMA]$_0$/[TTC-CTA]$_0$/[CuBr(dNbpy)$_2$]$_0$ = 50/1/1. This polymerization showed no MMA conversion within the first 0.5 hour and required 120 hours to reach 90% MMA conversion (Figure 3.9C and Figure 3.9D).
Figure 3.9: A) Vinyl conversions as a function of polymerization time; B) Overlaid SEC curves of the final product in series of polymerizations with feed ratios of \([\text{transmer } 1]/[\text{CuBr(dNbpy)}_2] = X/1\) at 65°C, \([\text{transmer } 1] = 0.75 \text{ mol L}^{-1}\), \(X = 10, 25, 50, 200\); C) Monomer conversion as a function of polymerization time; D) Evolution of SEC curves with \([\text{MMA}]/[\text{CTA}]/[\text{CuBr}]/[\text{dNbpy}] = 50/1/1/2\) in toluene under 65°C.

To increase the polymerization rate, an alternative method was applied to use an ATRP inimer BIEM in the concurrent ATRP/RAFT system. The inimer functioning as an initiator could provide a high concentration of radicals via activation and chain transfer processes. As shown in Figure 3.6A, the polymerization under \([\text{transmer } 1]/[\text{BIEM}]/[\text{CuBr(dNbpy)}_2] = 50/1/1\) at 65°C in toluene reached 99% conversion within 15 hours.
50 hours (Table 3.1, entry 14), showing a faster polymerization than that without BIEM. Consequently, the polymerization produced high molecular weight ($M_{n,\text{MALLS}} = 635.5$ k) in 5 days instead of two weeks (Figure 3.10).

![Figure 3.10: Overlaid SEC curves from concurrent ATRP/RAFT homopolymerization of \([\text{transmer 1}]_0/\text{BIEM}_0/[\text{CuBr(dNbpy)}_2]_0 = 50/1/1\) at 65°C, \([\text{transmer 1}]_0 = 0.75 \text{ mol L}^{-1}\).](image)

In addition to the high molecular weight, the branching density in hyperbranched polymers, i.e., the DB value, is essential and needs quantitative characterization. Following a recent method developed in our group, \(^6\) the structure of the hyperbranched polymers in the current studies was carefully determined using the inverse gated decoupled quantitative $^{13}\text{C}$ NMR spectroscopy. \(^1\) After careful peak
assignments in the $^{13}$C NMR spectra with the assistance of heteronuclear single-quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) spectroscopy (Figure 3.11A and Figure 3.11B), integration of the peaks in Figure 3.11C was applied to calculate the DB of the hyperbranched polymer (TABLE 3.1, entry 10). The number fraction of $B^*$ subunit was determined as $f_{B^*} = N_{B^*}/(N_{B^*} + N_b) = 0.81$, corresponding to the reactivity ratio $r = k_{A^*}/k_{B^*} = (\text{conv}_{A} + f_{B^*} - 1)/(-\ln f_{B^*} + f_{B^*} - 1) = 40.6$ and the DB = 0.30. The same calculation method was also applied to the purified hyperbranched polymers produced by RAFT homopolymerization of transmer 1 with PEG-azo initiator (Table 3.1, entry 3) and the ATRP/RAFT polymerization using both CuBr/(dNbpy)$_2$ and inimer BIEM (Table 3.1, entry 14), showing similar DB values for all these three systems. Thus, the simple addition of small amounts of CuBr/(dNbpy)$_2$ catalyst with optional inimers avoided the use of thermal initiator and significantly improved the molecular weight of the hyperbranched polymers in the homopolymerization of transmers.
Figure 3.11: A) HSQC and B) HMBC spectra of purified hyperbranched polymer synthesized with feed ratios of [transmer 1]/[CuBr(dNbpy)2] = 50/1 at 65°C (Table 3.1, entry 12); C) Inverse gated decoupled 13C NMR spectrum of hyperbranched polymer. (Pages 95-96)
Figure S5. HMBC

C2
C3
C1 & C4
Q & W Y, K & M
X
B

A

B

C1 & C4
C3
C2
3.4 Conclusions

We report the first synthesis of hyperbranched polymers with very high molecular weights in the homopolymerization of transmer. Traditional RAFT polymerization of transmer using PEG-azo thermal initiators produced relatively low-molecular-weight hyperbranched polymers because the termination reactions mainly occurred between propagating radicals and primary radicals. These termination reactions by losing TTC groups could introduce disproportionation vinyl groups and PEG initiator fragments into polymers, but contributed little to the molecular weight of
hyperbranched polymers. In contrast, the activation of TTC moieties using CuBr/(dNbpy)$_2$ catalyst avoided the use of any thermal initiator and eliminated the presence of primary radicals in the system. The concurrent ATRP/RAFT polymerization of transmer 1 produced hyperbranched polymers with over half-a-million molecular weight and high DB = 0.30. Further optimization by adding small amount of ATRP inimers into the system provided a stable radical concentration and resulted in a faster polymerization to produce high-molecular-weight polymers. These results highlight the importance of initiation technique in the homopolymerization of transmers to produce hyperbranched polymers with high molecular weights.

3.5 Acknowledgments

I would like to thank Dr. Yi Shi, Robert W. Graff, and Xiaosong Cao for their invaluable helps including polymerization conditions optimization, data interpretation, and transmer synthesis (Dr. Yi Shi).

3.6 References


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CHAPTER 4:
ONE-POT SYNTHESIS OF UNIFORM HYPERBRANCHED POLYMERS VIA
COPOLYMERIZATION OF TRANSMER AND ATRP INIMER IN MICROEMULSION

4.1 Introduction

Hyperbranched polymers and dendrimers are highly branched polymers with physical/chemical properties that are vastly different from their linear analogues. Highly branched polymers have potential applications such as drug-delivery vehicles, catalytic supports, and viscosity modifiers. However, the multistep synthesis and purifications between each step make dendrimer synthesis a costly and time-consuming process. In the past decades, hyperbranched polymers are catching more and more attestation due to their effortless one-pot synthesis, expanded compatibility with diversified functionality, and similarity to dendrimers in the architectural perspective. Hyperbranched polymers are commonly synthesized in bulk or solution via either step-growth polymerization of ABₙ monomer (containing one A group and f (≥2) B groups) or SCVP of AB⁺ inimer (containing initiator fragment B⁺ and monomer vinyl group A in one molecule). However, in both cases, the growth of hyperbranched polymers is accompanied by random polymer-polymer reactions in the continuous reaction media and finally results in polymers with lack of control over structural uniformity, i.e., MWD.
SCVP of AB* inimers enabled the use of vinyl monomers for a convenient, one-pot synthesis of hyperbranched vinyl polymers. In an ideal SCVP process, living polymerization systems are preferred in order to avoid cross-linking reactions. So far, cationic,4,5 anionic,6 group transfer,7,8 CRP,9,10 and processes have been employed. Among these “living” polymerization techniques the CRP including ATRP,3,11 NMP,12 and RAFT polymerization,2,13-18 were mostly utilized for the hyperbranched polymer synthesis. However, all of these methods presented undesirable structures with broad MWD,19 mainly due to the random polymer-polymer coupling reactions occurring in the continuous reaction media.4,20

To solve this problem, our group developed a new approach to synthesize hyperbranched polymers from AB* inimer by AGET ATRP with both high molecular weight and narrow MWD using microemulsion.21 So far, this robust technique has only been applied in ATRP of vinyl inimers with halogen initiating sites.20-23 It is desired to expand this novel method to cover broader application with diversified polymerization systems, e.g., RAFT polymerization, which offers compatibility with more functionalities. With this intention, we in this contribution for the first time report the use of microemulsion in regulating hyperbranched polymer structures via a one-pot polymerization of transmer in microemulsion. The conventional RAFT polymerization azo initiator was replaced by a new type of initiation system, which is the AGET ATRP initiation combination of inimer (alkyl bromide vinyl monomer) and copper/ligand catalyst. This rational choice of radical source guaranteed the absence of dead chain ends, fast initiation and polymerization, and continuous radical supply in the reacting
nanospace. Two types of trithiocarbonate transmers with methyl methacrylate and acrylate vinyl groups were designed and used to carry out the microemulsion polymerization. Consequently, the obtained hyperbranched polymer showed narrow MWD and hydrodynamic size ($D_h$) similar to that of nanoparticles (Scheme 4.1).

![Scheme 4.1. Microemulsion Polymerization of transmers in: an effective means to get one polymer within discrete nanospace.](image)

4.2 Experimental

4.2.1 Materials

All chemicals and solvents, including CuBr₂ (98%, Aldrich), sodium ascorbate (NaAs), and polyoxyethylene(20) oleyl ether (Brij 98, Alfa Aesar, 98%), carbon disulfide (Alfa Aesar, 98%), butanethiol (Alfa Aesar, 98%), 2-bromoisobutyric acid (Alfa Aesar, 98%), acetone (BDH chemicals, 98%), 2-hydroxyethyl methacrylate (HEMA, Sigma-
106

Aldrich, 98%), 2-hydroxyethyl acrylate (HEA, Sigma-Aldrich, 97%), 2-bromopropionyl bromide (Sigma-Aldrich, 98%), α-bromoisobutyryl bromide (Sigma-Aldrich, 98%), chloromethyl-4-vinylbenzene (Alfa Aesar, 98%), pyridine (Sigma-Aldrich, 99.8%), 4,4’-dinonyl-2,2’-dipyridyl (dNbpy, Sigma-Aldrich, ≥ 99%), 4-3-(3-dimethylaminopropyl)-1-ethyl-carbodiimide hydrochloride (EDC-HCl, Chem-Impex), 4-(dimethylamino) pyridine (DMAP, Sigma-Aldrich, 99%), glacial acetic acid dichloromethane (DCM, Sigma-Aldrich, >99.5%), sodium hydroxide (Sigma-Aldrich, 99.8%), poly(ethylene glycol) methyl ether methacrylate average Mn 300 (OEGMA300) (Sigma-Aldrich, 99.8%) was passed through basic aluminum column to remove inhibitors, 4-vinyl pyridine (4VP), (Sigma-Aldrich, 99.8%) and methacrylic acid (MAA) were distilled under reduced pressure to remove inhibitor. CuBr (98%, Aldrich) was purified by stirring in acetic acid overnight followed by washing with methanol and dried in vacuum oven under for overnight. Transmers were synthesized according to reported methods.24

4.2.2 Characterization

The size of the samples was determined by dynamic light scattering (DLS) equipped with a Zetasizer Nano-ZS (He-Ne laser wavelength at 633nm) (Malvern Instruments, Malvern, UK). Nuclear magnetic resonance (NMR) spectroscopy was carried out on a Bruker DM × 400 spectrometer operated in the Fourier transform mode. After filtration through 0.45 µm PTFE filter, the polymer samples were separated by size exclusion chromatography (SEC) with tetrahydrofuran (THF) as mobile phase. The THF SEC was equipped with Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and
10^2 Å SDV columns) at 35 °C with THF flow rate = 1.00 ml/min, a differential refractive index (RI) detector (Wyatt Technology, Optilab T-rEX) using PSS WinGPC 7.5 software. The apparent molecular weights were calculated based on linear poly(methyl methacrylate) (PMMA) standards. The detectors employed to measure the absolute molecular weights of hyperbranched polymer in THF SEC were the RI detector and a multi-angle laser light scattering (MALLS) detector (Wyatt Technology, DAWN HELEOS II) with the light wavelength at 658 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology with the dn/dc = 0.11 mL/g for all polymethacrylate-based polymers.\(^{25,26}\) Degree of branching (DB) determination of hyperbranched polymers were made following a recently developed method developed in our group using the inverse gated decoupled quantitative \(^{13}\)C NMR spectroscopy.\(^{20,24}\)

4.2.3 Synthetic procedures

4.2.3.1 Synthesis of transmer 1 and transmer 2

2-((2-(((butylthio)carbonothioyl)thio)-2-methylpropanoyl)oxy)ethyl methacrylate (transmer 1), 2-((2-(((butylthio)carbonothioyl)thio)propanoyl)oxy)ethyl acrylate (transmer 2), 2-(2-Bromoisobutylryloxy) ethyl methacrylate (inimer 1), and 2-((2-bromopropanoyl)oxy)ethyl methacrylate (inimer 2) were synthesized as followed procedures.

Transmer 1 was prepared according to the previously reported literature procedures.\(^{24}\) 2-(Butylthio-carbonothioylthio)-2-methylpropanoic acid (compound 1) was firstly synthesized as followed: A solution of sodium hydroxide (2.64g, 66 mmol) in
45 mL of acetone/water mixture was added into N\textsubscript{2} protected acetone (60 mL). 1-Butane thiol (5.95g, 66 mmol) was added over 10 min and the mixture was stirred for 45 min with temperature maintained between 5 and 15 °C. Carbon disulfide (5.0g, 66 mmol) was then added over 15 min followed by 1 hour reaction before warmed up to room temperature and stirred for a further period of 1 hour. 2-Bromo-2-methyl propionic acid (11.0g, 66 mmol) was then slowly added and the mixture was stirred for 24 hour. The reaction mixture was then poured into water, which was followed by extraction with ethyl acetate. The combined extracts were dried with anhydrous MgSO\textsubscript{4} and filtered. The solvent was removed using a rotary evaporator. The crude product was recrystallized three times with hexanes to provide pure Compound 1 as a yellow color solid with yield: 70%. Transmer 1 was then synthesized as followed: to a 250 mL round-bottom flask were added sequentially with compound 1 (10.8 g, 40 mmol), HEMA (5.72 g, 44 mmol), EDC·HCl (17.4 g, 80 mmol), dry DCM (120 mL) and DMAP (2.16g, 17.7 mmol). The reaction mixture was allowed to be stirred at room temperature overnight before washed with water (2×50 mL) and brine (2×50 mL), and dried over MgSO\textsubscript{4}. The solvent was evaporated, and the remaining residual was purified by silica gel chromatography (hexanes/diethyl ether, 4:1 v/v) to give 12.4 g light yellow liquid of the targeted monomer (82% yield). \textsuperscript{1}H NMR (in CDCl\textsubscript{3}, δ, ppm): 0.81-0.88 (3H, \textit{H}_3C\textit{CH}_2\textit{CH}_2\textit{CH}_2), 1.32-1.28 (2H, \textit{CH}_3\textit{CH}_2\textit{CH}_2\textit{CH}_2), 1.52-1.58 (2H, \textit{CH}_3\textit{CH}_2\textit{CH}_2\textit{CH}_2), 1.61-1.65 (6H, SC(\textit{CH}_3)_2\textit{CH}_2\textit{COO}), 1.85-1.87(3H, \textit{CH}_3\textit{C}=\textit{CH}_2), 3.15-3.21(2H, \textit{CH}_3\textit{CH}_2\textit{CH}_2\textit{CH}_2), 4.26-4.30 (4H, O\textit{CH}_2\textit{CH}_2O), 5.4-6.2(2H, \textit{CH}_2=\textit{CCOO}). In the synthesis of transmer, 25 g of 2-bromopropanoic acid and 10.10 g of HEA were used in a procedure similar to that
described above providing a crude oil which was distilled at 105-110 °C (1 mmHg); purity was ca. 97%. ¹H NMR (CDCl₃, δ, ppm): 4.95−5.05 (1H), 3.64−4.08 (4H), 1.71−1.75 (1H), 1.24−1.37 (6H).

4.2.3.2 Synthesis of inimer 1 and inimer 2

Inimer 1 and inimer 2 were synthesized according to similar procedure. Briefly, A 100 mL round bottom flask was loaded with a magnetic stir bar, HEMA (12.13 mL, 0.10 mol), pyridine (8.60 mL, 0.11 mol), and 70 mL DCM, before being cooled to 0 °C in an ice bath. 2-Bromoisobutyrl bromide (12.36 mL, 0.10 mol) was dissolved in 15 mL DCM and added to the reaction mixture via addition funnel over 45 min. The reaction was kept cold for an additional 45 min before being warmed up to room temperature for an additional 3 hours. After the reaction, the solvent was removed under reduced pressure before the product was purified on a silica column (4:1 hexanes: ethyl acetate), obtaining 25.68 g clear oil (92% yield). ¹H NMR (in CDCl₃, δ, ppm): 6.07 (1H, \(\text{CH}_2=\text{C}(\text{CH}_3)\)), 5.52 (1H, \(\text{CH}_2=\text{C}(\text{CH}_3)\)), 4.35 (4H, \(\text{OCH}_2\text{CH}_2\text{O}\)), 1.88 (3H, \(\text{CH}_2=\text{C}(\text{CH}_3)\)), and 1.86 (6H, \(\text{C}(\text{CH}_3)_2\text{Br}\)). To produce inimer 2, a 250 mL round-bottom flask was loaded with a magnetic stir bar, HEA (6.5g, 6.06 mL, 0.05 mol), pyridine (4.75g, 4.83 mL, 0.055 mol), and 35 mL of dichloromethane (DCM), before being cooled to 0 °C in an ice bath. 2-bromopropanoyl bromide (10.8g, 5.2 mL, 0.05 mol) was dissolved in 15 mL of DCM and added to the reaction mixture via an syringe pump over 45 min. The reaction was kept cold for an additional 45 min before being warmed up to room temperature for an additional 3 h. After the reaction, the solvent was removed under reduced pressure
before the product was purified on a silica column (4:1 hexanes: ethyl acetate), obtaining 25.68 g of clear oil (92% yield). 1H NMR (in CDCl3, δ, ppm): 6.07 (1H, $\text{CH}_2$=$\text{C}$($\text{CH}_3$)), 5.52 (1H, $\text{CH}_2$=$\text{C}$($\text{CH}_3$)), 4.35 (4H, O$\text{CH}_2$$\text{CH}_2$O), 1.88 (3H, CH2=$\text{C}$($\text{CH}_3$), and 1.86 (6H, C($\text{CH}_3$)$_2$Br).

Figure 4.1: $^1$H NMR spectra of A) transmer 1; B) transmer 2; C) inimer 1; and D) inimer 2.
4.2.3.3 Polymerization of transmer 1 in solution with AIBN as initiator

Typical procedures for polymerization of transmer 1 with AIBN are briefly described, \([\text{transmer}]_0/\text{[AIBN]}_0 = 30/1\) in 40 wt % toluene. A clean and dry 10 ml schlenk flask was charged with transmer (0.5 g, 1.3 mmol), AIBN (7.3 mg, 0.044 mmol) and 0.35 g toluene. The flask was deoxygenated by four freeze-pump-thaw cycles. The flask was sealed with a glass stopper then evacuated and back-filled with nitrogen five times before it was immersed in an oil bath at 70 °C. After 24 hours, the reaction was stopped by exposure to air and dilution with THF, and the final polymer was obtained after precipitation into methanol and drying under vacuum overnight to allow dry hyperbranched polymer 1 (HB1 in Table 4.1).

4.2.3.4 Microemulsion polymerization of transmer 1 with initiation of AIBN

Microemulsion polymerization of transmer 1 with initiation of AIBN in microemulsion was carried out with \([\text{transmer 1}]_0/\text{[AIBN]}_0 = 50/1\), AIBN was premixed with transmer 1 and the mixture was emulsified by adding to the round bottom flask dropwise, the system was magnetically stirred open to air under room temperature until all oil droplets emulsified. The microemulsion was then capped by a rubber septum and bubbled by N2 for 30 min before the reaction was initiated by immersing in 65 °C oil bath (HB2 in Table 4.1).
4.2.3.5 Polymerization of transmer 1 with initiation of inimer 1 and copper catalyst in solution

The procedures for polymerization of transmer 1 with inimer 1 and copper catalyst in solution were similar solution polymerization of transmer 1 with AIBN as initiator: dNbpy and inimer 1 were added into the flask with transmer 1 and conducted four freeze-pump-thaw cycles. AIBN was replaced by and CuBr was added during the final freeze-pump-thaw cycle under the nitrogen flow (HB3 Table 4.1).

(vi) Microemulsion polymerization of transmer 1 and transmer 2 with initiation of inimers and copper catalyst

Two transmers (transmer 1 and transmer 2 in Scheme 4.1) with different vinyl groups and CTA groups were used in the microemulsion polymerization to produce hyperbranched polymers with initiation by inimers (inimer 1 for transmer 2 and inimer 2 for transmer 2 respectively) and copper catalyst. A typical procedure on polymerization of transmer 1 with transmer 1/[inimer 1]/[CuBr$_2$(dNbpy)$_2$]/[NaAs] = 50/1/1/0.5 is briefly described. In a disposable test tube, dNbpy and CuBr$_2$ were mixed in DCM at 40 °C for half an hour before addition of transmer 1 (0.25g in total) to the mixture. After evaporation of the DCM at 25 °C with air bubbling, the mixture was added dropwise to a solution of 1 g Brij98 in 12 g water over 60 minutes to form a transparent microemulsion. Meanwhile, the temperature was slowly stepped up to 65 °C and stabilized for less than 10 minutes before injection of NaAs solution in water to reduce the Cu(II) species and initiate the polymerization. During the polymerization, samples were withdrawn by long-needle syringe and dried in air for 1H NMR and SEC analysis.
The reaction was finally stopped after all vinyl conversion 100% determined by $^1$H NMR by exposure to air. The hyperbranched polymers were purified with precipitating into methanol three times to allow hyperbranched polymer 4 (HB4 in Table 4.1) The polymerization of transmer 2 was conducted with the same procedures to produce hyperbranched polymer 5 (HB5 in Table 4.1).

4.2.3.6 Hyperstar polymers synthesis

Typical procedures by using HB4 as MCTA are and OEGMA$_{300}$ as monomerare briefly described. A clean and dry 10 ml Schlenk flask was charged with HB4 (36.4 mg, 0.01 mmol TTC), AIBN (1.64 mg, 0.01mol), and OEGMA$_{300}$ (6 g, 0.02 mol) and capped with glass stopper. The flask was then deoxygenated by five freeze-pump-thaw cycles before immersing in an oil bath at 40 °C to start the reaction. Samples were taken at time intervals under the N$_2$ flow with syringe for DLS and $^1$H NMR measurement. For polymerization of other two monomers, 4VP (5.25 g, 0.05 mol) and MAA (4.3 g, 0.05 mol) were used. The reactions were stopped at 21% (OEGMA$_{300}$), 25% (4VP), and 23% (MAA) monomer conversion to avoid the ill-defined polymers due to the intermolecular coupling reaction.

4.3 Results and discussion

4.3.1 Comparison of polymerization of transmer 1 with different initiators and polymerization media: AIBN initiated polymerization in solution, AIBN initiated
polymerization in microemulsion, and inimer + copper catalyst initiated polymerization in microemulsion

Before conducting polymerization of transmers in microemulsion with inimer + copper catalyst as initiators, three SCVPs of transmer 1 including 1) using AIBN as initiator in solution, 2) using AIBN as initiator in microemulsion, and 3) using inimer + copper catalyst as initiator in solution were performed as reference examples. Polymerization of transmer 1 in solution with AIBN produced hyperbranched polymer HB1 with low molecular weight ($M_{n,IR}=5,200$, $M_{\text{MALLS}} = 9,900$) and higher dispersity (PDI=1.97), the degree of branching (DB) was determined to be 0.28. This is in agreement with reported results that only low molecular weight and broad molecular weight distribution could be obtained through solution polymerization of transmers. Apparently, the low molecular weight and MWD would not allow a good result in microemulsion polymerization given that a regular microemulsion with latex sized around 10 nm would produce low-dispersity hyperbranched polymer with molecular weight at millions level as reported in literature.$^{20,23}$ To further prove this claim, the polymerization of transmer 1 with AIBN was carried out in microemulsion with similar latex dynamic size (12 nm) as reported in the ATRP microemulsion (Figure 4.2B). However, after pushing the reaction to no molecular weight change with further heating, i.e., end of polymerization, the produced HB2 only gave a slightly higher molecular weight ($M_{n,IR} = 12,000$, $M_{\text{MALLS}} = 22,800$) and more broad dispersity (PDI=2.13), as shown in Figure 4.2B. The DB of HB2 is similar to HB1 as 0.30. In addition, as another method to check the success of formation of one polymer per latex, the DLS
gave a smaller hydrodynamic size \( (D_{h,\text{THF}}) \) after dissolving the isolated polymer from microemulsion in THF which indicated small fractions formed in the latex particles instead of one single polymer particle. This fact brings a challenge for the polymerization of transmers in microemulsion targeting on uniform hyperbranched polymer synthesis which requires a complete vinyl conversion and exclusion of uncombined polymer species in each latex droplet. Tuning the \([\text{transmer}]_0/[^{\text{A}}\text{IBN}]_0\) ratio would not improve this scenario since more AIBN would cause faster and complete consumption of vinyl groups with the price of more non-polymerizable, while less AIBN initiator could not guarantee the complete consumption of vinyl groups.\(^{24}\) To avoid these two limits in the conventional RAFT polymerization of transmers, the replacement of azo thermal initiation with radical generation from the transmer itself provides a key. Most recently, our group reported the synthesis of hyperbranched polymers with high molecular weight (over half a million) in the homopolymerization of trithiocarbonate transmer by using copper catalyst initiation in a solution base.\(^{24}\) The transmer 1 was here tested for homopolymerization using 2 mol % of CuBr at \([\text{transmer }1]_0/[\text{CuBr}(\text{dNbpy})_2]_0 = 50/1\) at 65 °C. During the polymerization, the SEC traces of hyperbranched polymers indicated a slow and steady increase of molecular weights over a 2 week reaction time and finally reached HB3 a molecular weight \(M_{n,MALLS} = 434,400\) represented the last sample that could be separated by the SEC columns (Figure 4.2D. A very slow polymerization kinetic was observed and it took weeks to hit a high molecular weight while a low fraction of inimer, e.g. 1% by mole, could improve this situation. A faster polymerization is beneficial for the stability of the microemulsion
and hence crucial for the control over the hyperbranched polymer MWD. Based on this, in the following discussion, a combination initiation system including ATRP inimers and copper catalyst was applied.

Figure 4.2: (A) Overlaid THF SEC curves of hyperbranched polymers during the solution polymerization with $[\text{transmer 1}]_0/[\text{AIBN}]_0 = 50/1$, 65 °C, $[\text{transmer 1}]_0 = 0.75 \text{ mol L}^{-1}$; (B) Overlaid THF SEC curves of hyperbranched polymers during the microemulsion polymerization with $[\text{transmer 1}]_0/[\text{AIBN}]_0 = 50/1$, 65 °C; (C) DLS curves of HB2 in latex before purification and in THF after purification with $[\text{transmer 1}]_0/[\text{AIBN}]_0 = 50/1$, 65 °C in microemulsion; (D) Overlaid THF SEC curves of hyperbranched polymers during the solution polymerization with $[\text{transmer 1}]_0/[\text{CuBr(dNbpys)}_2]_0 = 50/1$ at 65 °C and $[\text{transmer 1}]_0 = 0.75 \text{ mol L}^{-1}$. 
4.3.2 Microemulsion polymerization of transmer 1 with initiation of inimer and copper catalyst

Firstly, polymerization of transmer 1 in microemulsion was conducted at 65 °C with \([\text{transmer } 1]_0/[\text{inimer } 1]_0/[\text{CuBr}_2(\text{dNbpy})_2]_0/[\text{NaAs}]_0 = 100/1/1/0.5\). Microemulsion polymerization of transmer 1 showed a fast polymerization with the conversion of methacrylate double bonds reaching 98% within 30 min (Figure 4.3A), and the kinetic followed a similar pattern as reported in AGET ATRP of halogen carrying inimers.\(^{20}\) In contrast, it took days for the solution polymerization of transmer 1 to reach such a high molecular weight as aforementioned. The fast transmer 1 polymerization in the microemulsion droplets was mainly due to the concentration effect without dilution. Figure 4.3B shows the molecular weight evolution of hyperbranched polymers after removing most of the surfactant but with minimal polymer fractionation. It was found that polymer dispersity decreased along the vinyl group conversion from \(M_w/M_n \sim 3.1\) with \(~64\%\) vinyl conversion at 1 min to \(M_w/M_n \sim 1.2\) with \(~99\%\) vinyl conversion at 120 min (Figure 4.3C). This is in agreement of previously reported results in which only one single hyperbranched polymer could form in each latex droplet at complete conversion, and hence the dimension and uniformity of the hyperbranched polymers could be directly regulated by discrete droplets. Finally, HB4 after complete conversion exhibited a high molecular weight (\(M_{n,MALLS} = 701k\) and \(M_{n,RI} = 89.1k\), Table 4.1) and low dispersity (\(M_w/M_n = 1.2\)). The DLS measurements of the polymer in latex before purification and in THF after purification further supported the one polymer per latex droplet concept as
shown in Figure 4.3D that an increased $D_h$ was observed after dissolving HB4 in THF as compared to the of latexes in water.

Figure 4.3: (A) Dependence of transmer 1 conversion and $\ln([M_0]/[M])$ on reaction time determined by $^1$H NMR; (B) SEC traces of minimally purified HB polymers at different conversions; (C) Relative molecular weight and $M_w/M_n$ versus conversion of methacrylate groups; (D) DLS curves of HB in latex before purification and in THF after purification during the microemulsion polymerization with [transmer 1]₀/[inimer 1]₀/[CuBr₂(dNbp)₂]₀/[NaAs]₀ = 100/1/1/0.5.
Finally, the DB was determined by using the same method as discussed in chapter 3 according to the inverse gated decoupled quantitative $^{13}$C NMR spectroscopy as shown in Figure 4.4. After careful peak assignments in the $^{13}$C NMR spectra integration of the peaks in Figure 4.4 was applied to calculate the DB of the hyperbranched polymer. The number fraction of B* subunit was determined as $f_{B^*} = N_{B^*}/(N_{B^*} + N_b) = 0.83$, corresponding to the reactivity ratio $r = k_{A^*}/k_{B^*} = (\text{conv}_A + f_{B^*} - 1)/(-\ln f_{B^*} + f_{B^*} - 1) = 48.4$ and the DB $= 0.28$. 

Figure 4.4: Inverse gated decoupled $^{13}$C NMR spectrum of HB4.
TABLE 4.1
HYPERBRANCH POLYMERS SUMMARY

<table>
<thead>
<tr>
<th>polymer</th>
<th>medium</th>
<th>trans</th>
<th>initiator</th>
<th>$M_n$,$M_{n,\text{MALLS}}$</th>
<th>$M_n$,$M_{n,\text{RI}}$</th>
<th>$M_w$/$M_n$</th>
<th>$D_{h,\text{H}_2\text{O}}$</th>
<th>$D_{h,\text{THF}}$</th>
<th>CV</th>
<th>DB</th>
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<td>HB1</td>
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<td>AIBN</td>
<td>$9.9 \times 10^3$</td>
<td>$5.2 \times 10^3$</td>
<td>1.97</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.28</td>
</tr>
<tr>
<td>HB2</td>
<td>microemulsion</td>
<td>1</td>
<td>AIBN</td>
<td>$12.1 \times 10^3$</td>
<td>$22.3 \times 10^3$</td>
<td>2.13</td>
<td>13</td>
<td>6</td>
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<td>0.30</td>
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<td>-</td>
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<tr>
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<td>Inimer 1 + CuBr$_2$(dNbpy)$_2$</td>
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<td>2</td>
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<td>-</td>
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a Number-average molecular weight measured by THF SEC with MALLS detector. b Apparent number-average molecular weight and molecular weight distribution measured by SEC with RI detector, calibrated with linear PMMA standards and THF mobile phase.

Hydrodynamic diameter ($D_h$) and coefficient of variation (CV) determined by DLS using PMMA refractive index.

Degree of branching (DB) determined by NMR.
4.3.3 Microemulsion polymerization of transmer 2 with initiation of inimer and copper catalyst

Microemulsion polymerization of transmer 2 with inimer 2 and copper catalyst as initiator was carried out with the same condition as transmer 1. Briefly the polymerization was set up with ratio \([\text{transmer 2}]_0/\text{[inimer 2]}_0/[\text{CuBr}_2(\text{dNbpy})_2]_0/[\text{NaAs}]_0 = 100/1/1/0.5\) at 65 °C. The emulsification of transmer 2 was as successful as that of transmer 1 with similar \(D_{h,H_2O} = 12\) nm before initiating the polymerization as shown in Figure 4.5A. However, the \(D_{h,H_2O}\) of microemulsion latex experienced a slow increase before vinyl group conversion achieved 80% (Figure 4.5B). After that the \(D_{h,H_2O}\) was fixed and no further increase was observed. This is different from transmer 1 microemulsion polymerization which has absence of \(D_{h,H_2O}\) change during the whole polymerization. By comparing these two polymerization kinetics, it is obvious that polymerization of transmer 1 was faster than that of transmer 2 since polymerization of transmer 2 took 60 min to achieve a 98% vinyl conversion which transmer 1 only took 20 min. The slow polymerization of transmer 2 might cause the aggravation of polymerizing latex droplets. Nevertheless, the size change stopped after monomer conversion reached 80% which ended with a \(D_{h,H_2O} = 36\) nm and maintained a narrow latex droplet distribution (CV = 0.12). Figure 4.5C shows the molecular weight evolution of hyperbranched polymers after removing most of the surfactant but with minimal polymer fractionation. Although the slow polymerization gave a changed \(D_{h,H_2O}\), a much clear evolution of small polymer pieces combined into one single polymer kinetic could
be caught and presented as shown in Figure 4.5C. As expected, polymers with small molecular weight and broad molecular weight distribution were initially formed at low conversion. As the reaction progressed, the small fractions decreased and combined into a sharp and narrow distributed peak and finally only one single narrow peak represented the final product had only one polymer per micelles. Surprisingly, the $D_{h,H2O}$ increased in a fashion that allowed a good maintenance of the latex droplet dimension and uniformity which guaranteed the regulation of the molecular weight and dispersity of hyperbranched polymers. After purification of hyperbranched polymer HB5, the DLS in THF determined a $D_{h,THF} = 56$ nm and exhibited a high molecular weight ($M_{n,MALLS} = 2,300,400$ and $M_{n,RI} = 383,300$) and low dispersity ($M_w/M_n = 1.28$).
Figure 4.5: (A) Dependence of transmer 2 conversion on reaction time determined by $^1$H NMR; (B) $D_h$ of micelles versus conversion of acrylate groups during the reaction; (C) SEC traces of minimally purified HB polymers at different conversions; (D) DLS curves of HB in latex before purification and in THF after purification during the microemulsion polymerization with [transmer 2]$_0$/[inimer 2]$_0$/[CuBr$_2$(dNbpy)$_2$]$_0$/[NaAs]$_0$ = 100/1/1/0.5 at 65 °C.

4.3.4 Hyperstar polymer synthesis

The synthesized hyperbranched polymer containing numerous terminal TTC groups can be used as a multifunctional MCTA for polymerization of another monomer
to produce a hyperstar. To test this concept, the produced HB4 was used as the MCTA to produce core-shell structured amphiphilic hyperstar polymer through polymerization with three water-soluble monomers OEGMA\textsubscript{300}, 4VP, and MAA. The hyperstar polymers produced were named as HS1, HS2, and HS3. As shown in Figure 4.6. The $D_h$ of the hyperstar polymers increased and maintained a monomodal distribution until stopping the reaction at a low monomer (~20%). It is worthy to mention that low monomer conversion is essential for bulk/solution-based chain extension of hyperbranched polymers to produce hyperstar polymers as discussed in Chapter 2.

![Figure 4.6: Hydrodynamic diameters ($D_h$) of (A) HB and hyperstar HS1; (B) HB and hyperstar HS2; (C) HB and hyperstar HS3.](image)
4.4 Conclusions and outlooks

In summary, we successfully achieved one-pot polymerization of transmers in microemulsion to produce hyperbranched polymers with both high molecular weight and uniform size. The polymer-polymer reactions were successfully confined within discrete nanoparticles in the microemulsion. Two types of transmers including methacrylate-based and acrylate-based transmers were tested and the obtained hyperbranched polymers containing thousands of transmer units were successfully applied as multifunctional MCTAs for producing hyperstar polymers via bulk chain extension polymerization under low monomer conversions.

4.5 References


APPENDIX A:

DEVELOPING RECYCLABLE PH-RESPONSIVE MAGNETIC NANOPARTICLES FOR OIL-WATER SEPARATION

A.1 Abstract

Hybrid magnetic nanoparticles (MNPs) with well-defined core-shell structure, pH-tunable interfacial activity and strong magnetic responsiveness were developed as recyclable stabilizers for oil-water separation. The Fe₃O₄ magnetic core was synthesized using a solvothermal method involving hydrolysis of Fe(II) and Fe(III) salts in basic condition, followed by surface-initiated atom transfer radical polymerization (SI-ATRP) of dimethylaminoethyl methacrylate to grow the PDMAEMA shell. The magnetic core allowed rapid separation of the oil droplets from emulsions under external magnetic field, while the pH-responsive polymer shell offered the hybrid MNPs tunable interfacial activity to form and break Pickering emulsion reversibly for recyclable use of the hybrid MNPs. Results showed that MNPs with longer PDMAEMA arms exhibited broader suitable pH range to form Pickering emulsion, but slower magnetic responsiveness. An optimized sample MNP3 with DP of PDMAEMA ca. 65 was screened out and tested to

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prove efficient separation of diesel emulsion droplets from water and the recyclability of the hybrid MNPs.

A.2 Introduction

Core-shell structured inorganic/organic hybrid nanoparticles have attracted ever increasing attentions due to their fascinating properties and functions when combining both inorganic and organic compositions into one entity \(^1,2\). These hybrid nanoobjects are often prepared using one of two strategies: a “grafting to” method \(^3-5\) by tethering polymer chains onto the inorganic particles and a “grafting from” method \(^6-10\) by growing polymer chains from the initiating sites on the particle surface. The polymeric shell in the hybrid materials not only protects the inorganic core from the environment and prevents particle aggregation \(^11-16\), but also renders the materials novel properties, such as tunable surface polarity and stimuli-responsiveness toward environmental change \(^3,17-20\).

Depending on the composition and length of the polymer arms, lots of hybrid nanoparticles show property of being able to assemble at the oil-water interface and therefore function as particulate stabilizers to form Pickering emulsions \(^21-25\). Although the formation of Pickering emulsion, such as the oil-in-water system, has been extensively reported using various types of polymeric and inorganic nanoparticles, such as silica nanoparticles \(^24,26,27\), clays \(^28,29\), microgels \(^24,30,31\), and polymeric latexes \(^32,33\), few studies have directly used hybrid nanoparticles with inorganic core and polymer shell to form Pickering emulsions \(^21,22,25,34\).
Efficient separation of oil from produced water streams represents an important process in petroleum industry. Current practices in industry use either gravity separator or metal mesh to separate oil from water. However, the generated water effluent often contains micrometer-sized oil droplets dispersed in water, forming a stable oil-in-water emulsion even without any stabilizer. Further reduction of oil content in this water effluent becomes fairly difficult and may cause significant concerns to environment and public health. To address this challenge, hybrid nanoparticles that contain a superparamagnetic core and a stimuli-responsive polymer shell become a desired solution since they can efficiently and reversibly adhere to the dispersed oil droplets in the emulsion. When applying an external magnetic field, the interface-adhered magnetic particles allow facile separation of oil droplets from the water phase. The superparamagnetic particles have negligible remnant magnetization avoids their aggregation, both during storage and after magnetic field treatment. Meanwhile, the use of stimuli-responsive polymer (sensitive to temperature, pH, electric fields etc.) as shell can break the concentrated Pickering emulsion after magnetic separation on demand, to finally recover the hybrid nanoparticles for a second round of separation. In addition, tethered polymeric materials on the MNPs give them antifouling properties and provide steric repulsion keeping particles apart from one another. Recently, Schmidt et al.  reported the use of superparamagnetic nanoparticles coated with polystyrene arms as the stabilizers for the preparation of cyclohexane-in-water Pickering emulsions, which were easily destabilized under magnetic heating via AC magnetic field treatment. Richtering et al. used Fe$_3$O$_4$@poly(N-isopropyl acrylamide) microgels that
contained magnetic core and thermo-responsive polymer shell to alter the toluene-in-water emulsion stability under an oscillating magnetic field to separate oil from water. Peng et al.\textsuperscript{41} reported the use of core-shell structured magnetic nanoparticles as magnetic separators to destabilize water-in-oil inverse emulsion and separate water from oil. However, to the best of our knowledge, no study so far has reported the use of pH and magnetic dual responsive nanoparticles as recyclable stabilizers for efficient oil-water separation.

In this contribution, we designed a core-shell structured hybrid magnetic nanoparticle (MNP) for effective separation of emulsified oil droplets (several to tens of microns in size) from water, which cannot be easily achieved using either gravity plate separator\textsuperscript{46} or membrane techniques.\textsuperscript{36} The hybrid MNPs contained a cluster of magnetic nanoparticles as the core and poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) as arm, showing dual stimuli-responsiveness to both external magnetic field and environmental pH. The sensitivity of polymer arms to pH could alter the surface polarity of the MNPs to reversibly form and break the oil-in-water Pickering emulsion. A complete cycle of the separation of emulsified oil from water is illustrated in four steps (Scheme A1) when diesel was used as an example of the hydrophobic oils. An emulsion that contained 2.5 wt\% of diesel droplets in water with no stabilizer showed high stability over weeks. In the first step, addition of an MNP stock solution into the emulsion under a proper pH allowed the adsorption of the MNPs to the diesel-water interface and formed a Pickering emulsion without altering the size of oil droplets. Second, applying an external magnetic field quickly dragged and concentrated
the MNP-coated oil droplets from water and achieved a recovery of 90 wt% of water by
decantation. Third, decreasing the water pH in the concentrated diesel-in-water
emulsion destabilized the oil droplets and separated the oil from the MNP-dispersed
aqueous phase. In the last step, the MNP aqueous dispersion was recovered after
separation from the diesel oil and reused in a second round of oil separation from
water.

Scheme A 1: Application of pH-responsive magnetic nanoparticles
(MNPs) as recyclable stabilizers for oil-water separation.

A.3 Experimental

A.3.1 Materials

All these chemicals and solvents were purchased and used as received:
FeSO₄·H₂O (96%, ScholAR Chemistry), FeCl₃·6H₂O (96%, ScholAR Chemistry), trisodium
citrate (99%, Alfa Aesar) and Sodium acetate (99%, Alfa Aesar), tetraethoxysilane (TEOS,
(99.0%, BDH Chemical), toluene (HPLC grade, JC.Baker), ethanol (HPLC grade, Aldrich), CuBr₂ (99%, Aldrich), 2-bromoisobutyryl bromide (97%, Aldrich), pyridine (97%, Aldrich), NaOH (99%, Aldrich), HCl (37 wt%, Aldrich), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HETEMA, 97%, Aldrich). Diesel was purchased from gas pump of Martin’s gas station at 2081 S Bend Ave South Bend, IN 46637. 2,2’-Dimethylaminoethyl methacrylate (DMAEMA, 99%, Polyscience Inc.) was purified by passing through basic alumina column to remove inhibitor. CuBr (99 %, Sigma-Aldrich) was purified using a modified literature procedure, namely washing with glacial acetic acid under 36 °C overnight followed by filtration and rinsing with methanol three times and dry in vacuum oven.

A.3.2 Characterization

Samples in transmission electron microscopy (TEM) characterization were prepared by drop casting dilute dispersions of Fe₃O₄ nanoclusters in ethanol, MP@SiO₂-Br in acetone, and MP@PDMAEMA MNPs in acetone on copper grids, and imaged using a JEOL 2010 transmission electron microscope under acceleration voltage 200kV. The magnetic property was characterized using a MPMS® superconducting quantum interference device (SQUID, Quantum Design, San Diego, CA). The hydrodynamic size and zeta potential distribution of the samples were determined by dynamic light scattering (DLS) equipped with a Zetasizer Nano-ZS (He-Ne laser wavelength at 633 nm) and an auto-titrator (Malvern Instruments, Malvern, UK). The apparent molecular
weights of detached PDMAEMA chains were determined by SEC (Waters) with DMF as eluent using linear poly(methyl methacrylate) (PMMA) as polymer standards. Thermogravimetric analyses were carried out using a TGA/DSC-1(Mettler Toledo) instrument. The MP@PDMAEMA hybrid MNPs were heated from 50 °C to 800 °C at a scanning rate of 10 °C/min in N₂.

A.3.3 Synthesis procedures

A.3.3.1 Synthesis of Fe₃O₄ nanoparticles

The procedures for the synthesis of Fe₃O₄ MPs were according to literature. In brief, 1.20 g of FeCl₃·6H₂O and 0.24 g of trisodium citrate were dissolved in ethylene glycol/ethanol (30 mL/3.3 mL) solution followed by addition of 1.6 g of sodium acetate under vigorous stirring within 5 minutes. The resultant mixture was then transferred to a teflon-lined stainless-steel autoclave (with a capacity of 40 mL) and reacted at 200 °C for 10 h. After that, the autoclave was cooled down to room temperature. The as-made black products were thoroughly washed with ethanol and deionized water three times, respectively, and finally vacuum-dried.

A.3.3.2 Synthesis of amine-functionalized MP@SiO₂-NH₂ nanoparticles

MP@SiO₂-OH was prepared through the coating of the silica layer onto the magnetic MNPs by a sol-gel method. 1 g of Fe₃O₄ seeds were suspended in the mixture of 400 mL of ethanol, 50 mL of deionized water, and 12.5 mL of 25 wt % ammonium hydroxide aqueous solution. Then, 3 mL of TEOS was added under the mechanical stirring together with the sonication at room temperature for 4.5 h. APTES (0.1 mL)
diluted in 3 mL ethanol was then added by syringe pump in 30 min. The reaction mixture was stirred for 12 h. The resulted MP@SiO$_2$-NH$_2$ particles were purified by three cycles of centrifugation, decantation, and redispersion in ethanol with ultra-sonication. The products were dried in a vacuum oven until constant weight.

A.3.3.3 Synthesis of Br-functionalized MP@SiO$_2$-Br nanoparticles

The amine-functionalized MP@SiO$_2$-NH$_2$ (2 g) was mixed with dry toluene (250mL) and dry pyridine (5 mL) in a flask. After cooled to 0 °C in an ice bath, 2-bromoisobutyryl bromide (5 mL, 40 mmol) was added dropwise. The solution was then stirred at 0 °C for 0.5 h at room temperature for 12 h. The nanoparticles were purified by following similar procedures as those described for the synthesis of MP@SiO$_2$-NH$_2$ nanoparticles. The final product was dried in a vacuum oven overnight at 50 °C.

A.3.3.4 SI-ATRP of DMAEMA from MP@SiO$_2$-Br

MP@SiO$_2$-Br (2 g), HEMTETA (40 µL), DMAEMA (1.0 g), acetone (3 mL) and anisole (30µL) were added to a schlenk flask. The mixture was sonicated for 1 min before sealed and deoxygenated by three freeze-pump-thaw cycles. In the frozen state, CuBr (14 mg) and CuB$_2$ (5 mg) were added under protection of N$_2$ flow. The flask was then subjected to two additional freeze-pump-N$_2$ backfilling cycles before thawed at room temperature. Since the mixture with MP@SiO$_2$-Br cannot be stirred using a magnetic stir bar, the schlenk flask was connected to a motor equipped with a clamp before immersed in a water bath (40 °C). Under protection of flowing N$_2$, 0.4 ml of sample was taken out of the reactor at five timed intervals. A small fraction of each
sample was diluted with acetone to determine the monomer conversion using GC, while the remained samples were purified subjected to repeated magnetic separation and re-dispersion in ethanol for three times. The obtained MP@PDMAEMA hybrid MNPs were dissolved in DI water for future use. The reaction was finally stopped after 5 days.

A.3.3.5 PDMAEMA chain cleavage from the hybrid MNPs surface

Typical procedures for PDMAEMA chain cleavage from the particle surface are briefly described. The hybrid MNPs was added into 24% HF aqueous solution in a plastic centrifuge tube and stirred at room temperature for 6 h. After reaction, the insoluble was isolated via centrifugation. The aqueous layer including PDMAEMA was carefully decanted and transferred to a second plastic centrifuge tube. The isolated solids were washed by 24% HF aqueous solution followed by centrifugation to extract the residual PDMAEMA three times. The centrifuge tube with PDMAEMA solution was then left in hood to dry. After this, the isolated solid was dried in vacuum oven under 60°C overnight to get PDMAEMA.

A.4 Results and Discussion

![Scheme A 2: Synthetic scheme of the hybrid MNPs.](image)
A.4.1 Pickering emulsion preparation from three oils

Three types of oil were used to make Pickering emulsion: diesel, \(n\)-dodecane and anisole. MP@PDMAEMA hybrid MNPs were first dispersed in DI water with 0.4 g/mL. The water/oil ratio was 1/1 by volume with 3 mL in total. The MP@PDMAEMA hybrid MNP stock solution with particle fraction of about 1 % by weight of oil was added to the water with adjusted pHs tuned by 0.1M NaOH or 0.1M HCl solutions. Pickering emulsions were formed via hand shaking the samples.

A.4.2 Oil droplets separation and recycling of hybrid MNPs

A 3 mL diesel-in-water stock emulsion containing 2.5 % of diesel by volume was made from powerful sonication by 5 min sonication (Branson Sonifier 450). The emulsion without any stabilizer was stable over 3 weeks without significant phase separation. MNP3 with pre-determined concentration stock solution (10 µL, 0.4 g/mL) was added to the diesel-in-water emulsion in water under pH = 8.1. The emulsion was shaken by hand for one minute to let the MNP3 assemble onto the diesel/water interface. Upon applying an external magnetic field, the MNP-coated diesel droplets were removed to the vial wall. The water after this treatment was transparent and colorless which was easily collected by decanting and separated from the concentrated diesel oil. Addition of HCl solution (0.1M) into the concentrated MNP-coated diesel droplets destabilized the emulsion and produced a bilayer mixture with diesel on top of the MNP dispersed aqueous phase. The MNP aqueous dispersion in the bottom layer was subsequently pipette out and treated with 0.1 M NaOH solution to tune the pH back
to 8.1 before added to a second batch of diesel-water emulsion for separation. This recycling procedure was conducted for six rounds with no change in MNP morphology and oil separation efficiency.

A.4.3 Synthesis of the core-shell structured MNPs

Hybrid MNPs containing a cluster of superparamagnetic Fe$_3$O$_4$ nanoparticles as core, a thin layer of SiO$_2$ middle shell and a pH-responsive PDMAEMA outer shell were successfully synthesized in four steps, as illustrated in Scheme A2. First, magnetic clusters (termed as MP) containing lots of spherical superparamagnetic Fe$_3$O$_4$ nanoparticles with size around 20 nm (Figure A1D) were synthesized using a solvothermal method according to the literature.$^{50,51}$ The produced MPs showing an average diameter of 112 nm in TEM were then coated with a thin layer of silica to improve the stability of the MPs in dispersion. These produced MP@SiO$_2$-OH nanoparticles containing hydroxyl groups on the silica surface were subsequently modified using 3-APTES to make MP@SiO$_2$-NH$_2$ followed by reaction with 2-bromoisobutyryl bromide to introduce bromine initiating groups, producing MP@SiO$_2$-Br.$^{52}$ Finally, surface-initiated atom transfer radical polymerization (SI-ATRP)$^{6,53-58}$ of DMAEMA was applied to grow polymer shells. Samples were taken out of the reactor at timed intervals with different DMAEMA conversions to obtain a series of 6 MNPs with various PDMAEMA arm lengths. These MNPs are designated as MP@PDMAEMA$_x$, in which the subscript “x” represents the average degree of polymerization (DP) of the PDMAEMA arms in each sample: MP@PDMAEMA$_{35}$, MP@PDMAEMA$_{53}$,
MP@PDMAEMA$_{65}$, MP@PDMAEMA$_{156}$, MP@PDMAEMA$_{223}$ and MP@PDMAEMA$_{288}$, which was determined in DMF size exclusion chromatography (SEC) based on linear poly(methyl methacrylate) (PMMA) standards after detaching the PDMAEMA arms from the MNPs. In the following discussion, these six hybrid MNPs are referred as MNP1, MNP2, MNP3, MNP4, MNP5 and MNP6, respectively (Table A1).

Figure A1 shows representative TEM images of the bare MP (Figure A1A), MP@SiO$_2$-OH (Figure A1B) and MNP3 (MP@PDMAEMA$_{65}$) (Figures A1C, A1D) nanoparticles. The hybrid MNP3 exhibited a layered structure with a spherical magnetic cluster core (~110 nm diameter), a SiO$_2$ middle layer (~15 nm thickness) and a PDMAEMA arm layer (~15 nm thickness). With the increase of DMAEMA conversions,
the produced MNPs showed an increased hydrodynamic diameters ranging from $D_h = 157$ nm to 298 nm, determined by DLS in water under pH = 7 (Figure A1A), indicating a successful synthesis of core-shell structured MNPs with tunable polymer arm lengths. After using HF solution to etch the silica layer, the PDMAEMA arms were cut off from the hybrid MNPs for characterization of molecular weights using DMF SEC (Figure A2B). All six PDMAEMA chains showed monomodal SEC chromatograms with narrow molecular weight distribution ($M_w/M_n = 1.2-1.3$).

Figure A 2: A) Hydrodynamic diameter of hybrid MNPs in water under pH 7; B) SEC traces of the detached PDMAEMA arms based on linear PMMA standards in DMF; C) TGA curves of the MP@SiO$_2$-NH$_2$, MP@SiO$_2$-Br and the hybrid MNPs with various polymer arm lengths; D) The magnetic hysteresis loops of bare MP, MP@SiO$_2$-Br and the hybrid MNPs with inset of digital pictures to show the magnetic responsiveness after dispersed in water.
Figure A2C shows the TGA results of hybrid nanoparticles. Before surface polymerization, there exists $\sim 0.4$ wt % difference in the weight retentions at 800 °C between amino- and 2-bromoisobutyrate-functionalized silica nanoparticles (Figure A2C), which represents the weight fraction of organic initiating groups in the MP@SiO$_2$-Br. After SI-ATRP of DMAEMA, significant weight loss of each MNP sample was observed in the TGA analysis, indicating the successful incorporation of PDMAEMA hairs on the MNPs. The contents of polymer fractions are summarized in Table A1. With the varied arm lengths, the weight losses of the hybrid MNPs in the TGA analysis varied from 4% in sample MNP1 to 20% in MNP6. Assuming a spherical geometry for silica coated Fe$_3$O$_4$ nanoparticles with volume $V = 4/3\pi r^3$ ($r = 70$ nm based on the TEM image) and a density $\rho_{\text{Fe}_3\text{O}_4@\text{Si}} = 3.45$ g/cm$^3$ (calculated from density of silica which is 2.65 g/cm$^3$, density of Fe$_3$O$_4$ which is 5 g/cm$^3$ and their volume ratio 1.06). The average mass of single silica coated Fe$_3$O$_4$ particle was calculated to be $4.96 \times 10^{-15}$ g. Assuming a spherical geometry for silica coated Fe$_3$O$_4$ nanoparticles with surface area $S = 4\pi r^2$, the average number of initiator on each MP@SiO$_2$-Br is $\sim 8.0 \times 10^4$ with initiator density $\sim 1.3$ initiator/nm$^2$. Using the weight retention at 800 °C for each sample and the $M_n$ of grafted PDMAEMA chains determined by SEC, the average number of grafted PDMAEMA chains on each MNP can be estimated to be $\sim 1.8 \times 10^{14}$. The grafting density of PDMAEMA chains at the surface of MNPs can be estimated to be $\sim 0.3$ polymer/nm$^2$. As the density of ATRP initiators is $\sim 1.3$ initiator/nm$^2$, the initiation efficiency for the surface-initiated ATRP of PDMAEMA is $\sim 22.5\%$. Derailed calculation could be found as followed:
1. Radius of the silica-coated Fe$_3$O$_4$@SiO$_2$: $r = 70$ nm from TEM;

2. Density of the silica-coated Fe$_3$O$_4$: $\rho_{Fe3O4@SiO2} = 3.57$ g/cm$^3$, calculated from the density of silica (2.07 g/cm$^3$)$^{59}$, density of Fe$_3$O$_4$ (5.18 g/cm$^3$)$^{60}$ and their volume ratio in Fe$_3$O$_4$@SiO$_2$ ($V_{SiO2}/V_{Fe3O4} = 0.51/0.49$)

3. Average volume of a single Fe$_3$O$_4$@SiO$_2$: $V = \frac{4}{3}\pi r^3 = 1.4 \times 10^6$ nm$^3$

4. Average surface area of a single Fe$_3$O$_4$@SiO$_2$: $S = 4\pi r^2 = 6.2 \times 10^4$ nm$^2$

5. Average mass of a single silica coated Fe$_3$O$_4$ particle as $M_{Fe3O4@SiO2} = 5.0 \times 10^{-15}$ g

6. Average number of grafted polymer chains per MFe$_3$O$_4$@SiO$_2$:

$$N = \frac{\text{Weight}_{polymer}}{\text{Weight}_{Fe3O4@SiO2}} \times \frac{M_{n,mPDMAEMA}}{M_{Fe3O4@SiO2}} \times N_A = 1.8 \times 10^4 \text{ chain/particle}, \text{ where } N_A \text{ is the Avogadro number;}$$

7. Grafting density of polymer chain /nm$^2$ on particle surface: $d = N/S \approx 0.3$ polymer chain/nm$^2$)
### TABLE A.1

**PHYSICAL PROPERTIES OF HYBRID MNPS**

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<th>DP $^a$</th>
<th>$M_{n,RI}$ $^a$</th>
<th>$M_w/M_n$ $^a$</th>
<th>$D_h$ $^b$ (nm)</th>
<th>CV $^b$</th>
<th>Polymer content $^c$ (wt%)</th>
<th>Magnetic saturation value $^d$ (emu/g)</th>
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<td>225</td>
<td>0.16</td>
<td>11.6</td>
<td>70.5</td>
</tr>
<tr>
<td>MNP5</td>
<td>223</td>
<td>35.1×10$^3$</td>
<td>1.33</td>
<td>267</td>
<td>0.19</td>
<td>15.1</td>
<td>66.7</td>
</tr>
<tr>
<td>MNP6</td>
<td>288</td>
<td>45.2×10$^3$</td>
<td>1.34</td>
<td>298</td>
<td>0.20</td>
<td>20.0</td>
<td>63.4</td>
</tr>
</tbody>
</table>

$^a$ Degree of polymerization (DP), apparent number-average molecular weight ($M_{n,RI}$) and molecular weight distribution ($M_w/M_n$) measured by DMF SEC with RI detector, calibrated with linear PMMA standards.

$^b$ $D_h$ and coefficient of variation (CV) of bare MPs (in acetone), MP@SiO$_2$-Br (in acetone) and MNPs (in pH = 7 water) were measured by DLS.

$^c$ Polymer weight fraction measured by TGA under $N_2$ at a heating rate of 10°C/min.

$^d$ Magnetic property characterized using an MPMS® SQUID system (Quantum Design, San Diego, CA).

#### A.4.4 Properties of core-shell structured MNPs

Magnetic property is one of the key features of the hybrid MNPs. To separate the emulsified oil droplets and recycle the hybrid MNPs, it is important that the hybrid MNPs are superparamagnetic with fast response to external magnetic field. The magnetic properties of bare MPs, MP@SiO$_2$-Br and the series of PDMAEMA-coated MNPs were determined using a SQUID magnetometer and the results are shown in Figure A2D with saturation magnetization values summarized in Table A1. All samples
exhibited no hysteresis of magnetism, indicating that the core was a cluster of superparamagnetic nanoparticles with size smaller than 30 nm.\textsuperscript{51,61,62} The bare MP showed a saturation magnetization of 85 emu/g and this value decreased with the incorporation of silica shell and PDMAEMA polymer arms. All hybrid MNPs showed magnetic responsiveness and could be effectively concentrated from their aqueous dispersions when using a magnet, as shown in the inset of Figure A2D.

The length of PDMAEMA arms determines the pH responsiveness of the MNPs. In general, the polymers tethered on a particle surface often show a hysteresis in transition from hydrated to dehydrated states when responding to environmental change.\textsuperscript{63} For instance, upon the increase of environmental pH, the surface hydrated PDMAEMA segments would deprotonate first to form a thin dehydrated layer and thus slow down the inner polymer’s responsiveness. This phenomenon becomes more significant in MNP samples with longer polymer arms, which are expected to show a broader pH range in transition than MNPs with shorter PDMAEMA arms when increasing the environmental pH. The hydrodynamic sizes and zeta potentials of these six hybrid MNPs at different pH values were tracked by DLS equipped with an auto-titrator. In Figure A3, all hybrid MNPs show a decreased hydrodynamic size with increased pH. When the environmental pH was around 7.1-7.2, close to the apparent pKa of linear PDMAEMA in water,\textsuperscript{64-66} a sharp decrease of hydrodynamic size was observed in all MNP samples, although the transition finished at various pH values, depending on the PDMAEMA arm lengths.
The transition of PDMAEMA arms from protonated state to deprotonated state with the increase of environmental pH was confirmed by the physical appearance of these aqueous dispersions, switching from low pH (well dispersed) to high pH (precipitates) as shown in the inset of Figure A3B. The titration of MNPs with different PDMAEMA arm lengths revealed a suitable pH range for each hybrid MNP, in which the PDMAEMA arms showed amphiphilic nature with partial protonation of the tertiary amine groups and overall positive zeta potential. It is expected that an MNP within this pH range can assemble at the oil-water interface within a short period of treatment time.
A.4.5 The pH and magnetic responsiveness of MNP-coated Pickering emulsion.

To confirm the suitability of the pH range for each MNP sample, all six MNPs (in aqueous stock dispersion with concentration of 0.4 g/mL) were tested to form diesel-in-water Pickering emulsion (2.5 wt% of diesel in water with 5 wt% of MNP to diesel) under different pH values. For example, MNP3 as the stabilizer was able to form stable diesel-in-water Pickering emulsions at any pH within the range from 7.1 to 8.5 (Figure A4) when the PDMAEMA arms in the MNP were partially protonated with a positive zeta potential (34.5 to 2.7 mV) and showed an amphiphilic surface property. Beyond this pH window, the MNP surface would be either too hydrophilic at lower pH or too hydrophobic at higher pH, thus couldn’t stabilize the diesel droplets in water. Correspondingly, the diesel and water mixture was in a bilayer appearance at pH < 7.0 and pH > 8.5 (Figure A4). Inset is the digital pictures showing the appearances of the diesel/water mixtures under different pHs.
### TABLE A.2

**EFFECT OF ARM LENGTH ON THE PH AND MAGNETIC RESPONSIVENESS OF MNPS**

<table>
<thead>
<tr>
<th>Samples</th>
<th>pH range</th>
<th>Zeta potential range</th>
<th>pH of measurement</th>
<th>Magnetic responsiveness (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNP1</td>
<td>7.1-7.6</td>
<td>32.4-3.5</td>
<td>7.3</td>
<td>21</td>
</tr>
<tr>
<td>MNP2</td>
<td>7.2-8.0</td>
<td>33.3-2.8</td>
<td>7.6</td>
<td>27</td>
</tr>
<tr>
<td>MNP3</td>
<td>7.2-8.5</td>
<td>34.5-2.7</td>
<td>8.1</td>
<td>42</td>
</tr>
<tr>
<td>MNP4</td>
<td>7.1-9.1</td>
<td>35.2-2.8</td>
<td>8.5</td>
<td>73</td>
</tr>
<tr>
<td>MNP5</td>
<td>7.1-9.3</td>
<td>36.0-3.1</td>
<td>8.9</td>
<td>91</td>
</tr>
<tr>
<td>MNP6</td>
<td>7.1-9.4</td>
<td>37.2-3.5</td>
<td>9.0</td>
<td>102</td>
</tr>
</tbody>
</table>

*\(^a\) The pH range, within which, MNPs could stabilize Pickering emulsion.*

*\(^b\) The zeta potential of each MNP with the listed pH range.*

*\(^c\) The pH value at which the MNP formed the most stable Pickering emulsion with minimal MNP in aqueous phase or precipitated out.*

*\(^d\) Time needed for MNP-coated diesel droplets to arrive to the scintillation vial wall.*

---

**Figure A 4:** Illustration of the effect of pH on the formation of diesel-in-water Pickering emulsion using MNP3 as stabilizer. Inset includes digital pictures of the diesel-in-water at various pHs.
To determine the magnetic responsiveness, each MNP at the optimized pH environment was used to form a 3 mL diesel-in-water emulsion in a 4 mL scintillation vial. Upon exposure to a magnet, the MNP-coated diesel droplets showed instantaneous response with unidirectional movement toward the vial wall. The time required to complete this separation for each Pickering emulsion was used to compare the magnetic responsiveness of the MNPs (Table A2). The magnetic responsiveness time decreased with the increased PDMAEMA arm length in the MNPs, in agreement to the trend of magnetic saturation values of the samples. The results in Table A2 demonstrate the trend that a MNP with longer arms exhibited a broader pH range suitable of forming Pickering emulsions, but slower magnetic responsiveness. The MNP1 with PDMAEMA$_{35}$ arms had the narrowest pH range of 0.4 (from 7.1 to 7.5), while the MNP6 with the longest PDMAEMA$_{288}$ arms had the broadest pH range of 2.3 (from 7.1 to 9.4). On the other hand, the time needed to remove the diesel droplets increased from 22 seconds using MNP1 to 102 seconds using MNP6. It is evident that there is a need to balance the effect of PDMAEMA arm length on these two counteracting properties and screen out the optimal sample for further study of diesel-water separation. Figure 5 shows the arm length effect on both pH range and magnetic responsiveness of the six MNP samples. The two curves crossed at DP = 90, representing an optimal PDMAEMA arm length with balanced effect. Of the six available hybrid MNPs, MNP3 with PDMAEMA arm of DP = 65, which was the closest value to the DP = 90, was thus selected for further study.
Figure A 5: The effect of PDMAEMA arm DP on the pH range and magnetic responsiveness of each MNP.

Figure A 6: Optical microscope images of 3 types of oil-in-water Pickering emulsion by using MNP3 as stabilizer. The ratios of oil to water were 1:1 by volume with 1 wt% of MNP3 to oil. The average sizes of oil droplets in the three Pickering emulsions were 149 µm, 85 µm and 56 µm, respectively.
The hybrid MNP3 demonstrated capacity to stabilize various hydrophobic oils in water and form stable Pickering emulsions. Figure A6 shows the optical microscopy images of the three Pickering emulsions at pH = 8.1 by using three representative hydrophobic oils (diesel from gas pump, aromatic anisole and aliphatic n-dodecane). All these Pickering emulsions were stable for at least 1 month without any coalescence based on visual observation. At the same time, increasing and decreasing the environmental pH across the suitable pH window can quickly form and break the Pickering emulsions. For instance, at pH 4, MNP3 couldn’t stabilize the diesel-water mixture with 1:1 volume ratio (totally 3 mL) to form the Pickering emulsion. Addition of 25 µL of 0.1 M of NaOH solution changed the pH to 7.9 and the mixture quickly formed Pickering emulsion after gentle shaking, showing stable oil droplets with average size of 149 µm. Further addition of 25 µL of 0.1 M of HCl solution into the stable diesel-in-water Pickering emulsion decreased the pH to 3 (out of the suitable window) and immediately destabilized the emulsion to form a bilayer mixture (Figure A7). The property of the MNP3 to fast form and break the diesel-in-water Pickering emulsion by simply tuning the pH is critical to achieve the recyclability of the hybrid MNPs in the oil-water separation.
Figure A 7: Reversible breaking and forming Pickering emulsion by tuning pH: a) pH = 4 MNPs stayed in aqueous layer; b) pH = 7.9 and Pickering emulsion formed; c) pH = 3 and Pickering emulsion broke.

A.4.6 Application of MNP3 for separation of emulsified diesel droplets from water.

A 3 mL diesel-in-water stock emulsion containing 2.5 % of diesel by volume was made from powerful sonication. The emulsion without any stabilizer was stable over 3 weeks without significant phase separation, representing a realistic analog of the water effluent after gravity plate separation. Optical microscopy image of the diesel droplets before treatment with hybrid MNP3 in Figure A8 reveals numerous emulsified diesel droplets with size less than 10 µm. After addition of 10 µL stock dispersion of MNP3 in water (concentration 0.4 g/mL) with pH = 8.1, the emulsion was still homogenous with no evident change of the droplet size. Upon applying an external magnetic field, the MNP-coated diesel droplets were removed to the vial wall and produced a continuous water phase. The water after this treatment was transparent and colorless, which could be easily separated from the concentrated diesel oil and collected by decantation. Addition of HCl solution (0.1M) into the concentrated MNP-coated diesel droplets
destabilized the emulsion and produced a bilayer mixture with diesel on top of the MNP dispersed aqueous phase. After decanting the oil out of the vial, the collected MNP dispersion was further treated with 0.1 M NaOH solution to tune the pH back to 8.1 before added to a second batch of diesel-water emulsion for separation. This recycling procedure was conducted for six rounds with no change in MNP morphology and oil separation efficiency. Figure A8 shows the six batches of clear water after separation of oils by using the same batch of hybrid MNPs. The hybrid MNPs have high recyclability and can be used to purify the diesel containing water at least six rounds without losing efficiency demonstrated by the absence of oil droplets in all optical microscopy images of the isolated water (Figure A8).
Figure A 8: Demonstration of the recyclable application of hybrid MNP3 in isolation of diesel droplets from prepared stock diesel/water emulsion. (The first row is the microscope images of the liquid in the scintillation vials in each step, the scale bar applies to all of the three pictures; the second row includes the digital pictures of the liquid appearances and the third row shows the digital pictures of the isolated water from different batches of diesel-containing water by recycling the same batch of MNP3, the fourth row includes Optical microscope pictures of the six batches of water after purification).
A.5 Conclusions

Well-defined hybrid MNPs that contained a magnetic cluster as core and densely grafted pH-responsive polymers as shell were used as recyclable stabilizers for oil-water separation. The magnetic core was synthesized via solvothermal hydrolysis of Fe(II) and Fe(III) salts in basic condition, and the surface-tethered PDMAEMA arms were produced via SI-ATRP of tertiary amine-containing DMAEMA. This rational design of dual-responsive MNPs allowed the separation of MNP-coated oil droplets from aqueous phase when applying external magnetic field. At the same time, the pH-responsive polymer arms could change polarity upon environmental pH, thus reversibly form and break the Pickering emulsion as demands to recover the MNPs. The produced hybrid MNPs had a uniform size and the polymer hair lengths could be easily varied depending on the conversions of DMAEMA monomer during the SI-ATRP. Results indicated that MNPs with longer polymer arms showed broader pH windows suitable for forming Pickering emulsion, but slower magnetic responsiveness. Overall, an optimized MNP sample MNP3 that contained PDMAEMA arms with average DP = 65 was screened out and tested to prove efficient separation of diesel emulsion droplets from water. The same batch of MNPs could be recycled and used for six times without losing the particle morphology and separation efficiency. It is expected that the development of this novel hybrid MNPs with dual responsiveness can offer a facile and environmentally friendly route for the treatment of oil contaminated water.
A.6 Acknowledgments

I would like to thank Dr. Han Xia for his assistance of the TGA analysis. Dr. Doyun Lee and Dr. Yi Shi should be acknowledged for their help in optimizing the surface-initiated ATRP conditions. I would also like to thank Xiang Li for his help of the magnetic property characterization.

A.7 References


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APPENDIX B:

SYNTHESIS OF HYPERBRANCHED POLYMERS VIA PHOTOINDUCED METAL-FREE ATOM TRANSFER RADICAL POLYMERIZATION

A.8 Introduction

Dendritic polymers have received considerable interest and found various applications in catalysis, biomaterials, microelectronics, and nanomedicines, due to their three-dimensional structure, cavernous interior, and large number of peripheral functionalities.1-8 Among them, dendrimers are the most well-defined synthetic polymer structures require a multistep reaction and the intermediate purification steps, which actually limits their commercial development. To circumvent the tedious multi-step synthesis, people are putting more and more attention to hyperbranched polymers due to the effortless one-pot polymerization. Hyperbranched polymers are generally prepared various an one-pot polymerizations, such as polymerization of AB\textsubscript{m} (m ≥2) monomers,\textsuperscript{9-28} copolymerization of A\textsubscript{n} and B\textsubscript{m} monomers (e.g., A\textsubscript{2} + B\textsubscript{3}),\textsuperscript{29-32} polymerization of divinyl or multivinyl cross-linkers,\textsuperscript{33-39} and SCVP of polymerizable initiators, often known as inimers. The last technique requires the use of controlled polymerization methods, such as CRP,\textsuperscript{40-50} living ionic polymerization,\textsuperscript{51-55} ROMP,\textsuperscript{56} and group transfer polymerization.\textsuperscript{57} As one of the most efficient CRPs, ATRP provides new avenues for the preparation of hyperbranched polymers from a large range of functional
monomers under moderate polymerization conditions in comparison with ionic polymerization.\textsuperscript{41-43,58-61} However, the use of copper catalyst and residual catalyst in the final hyperbranched-polymer materials limited the ATRP applications in industrial applications, especially for some electronic or biomaterials applications. It would be very desirable to develop an ATRP method for hyperbranched polymer synthesis that does not use transition metals catalysts.

A significant focus for polymer chemists since the initial discovery of ATRP has been directed toward lowering catalyst loadings and/or removal of residual metals. Although catalyst loadings can be decreased to parts per million (ppm) which meet the requirement for less demanding applications or can be removed by dialysis, precipitation, or filtration, people are still seeking a more ambitious solution to this grand challenge by developing a metal-free catalyst system for ATRP. The deadlock was broken by Hawker et.al, who reported a photoinduced metal-free ATRP of methyl methacrylate using 10-phenylphenothiazine (PH-PTZ) as an organic photocatalyst.\textsuperscript{62} Other phenothiazine derivatives, such as 10-(4-methoxyphenyl)-phenothiazine (4-MeOPh-PTZ) and 10-(1-naphthalenyl)-phenothiazine (Nap-PTZ), were also developed as organic photocatalysts for ATRP and RAFT polymerizations of various functional monomers.\textsuperscript{63} To the best of our knowledge, there was no literature reported the application of metal-free ATRP in preparation of hyperbranched polymers.

Herein, we for the first time studied the synthesis of hyperbranched polymers via photoinduced metal-free ATRP. Various inimers were employed to demonstrate the versatility of this method in preparation of hyperbranched polymers. Furthermore, a
microemulsion polymerization system was applied for the synthesis of hyperbranched polymers with photoinduced metal-free ATRP of imimers, the obtained hyperbranched polymers showed narrow molecular weight distribution and hydrodynamic size similar to that of nanoparticles (Scheme B1).

Scheme B 1. Hyperbranched polymer synthesis via photoinduced metal-free atom transfer radical polymerization in solution and microemulsion.

A.9 Experimental

A.9.1 Materials

All chemicals and solvents, including sodium tert-butoxide (NaOtBu), 2-hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl acrylate (HEA), α-bromoisobutyryl bromide (BIBB), 2-bromopropanoyl bromide (BPB), pyridine, phenothiazine, , anhydrous chlorobenzene, dioxane, dichloromethane (DCM) were purchased from Sigma Aldrich
and used as received. RuPhos and RuPhos Precatalyst were purchased from Strem Chemicals Inc.

A.9.2 Characterization

Nuclear magnetic resonance (NMR) spectroscopy was carried out on a Bruker DM × 500MHz spectrometer operated in the Fourier transform mode. After filtration through 0.45 µm PTFE filter, the polymer samples were separated by size exclusion chromatography (SEC) with THF/DMF as mobile phase (polymers from solution polymerization were characterized by DMF SEC and polymer from microemulsion was subjected to THF SEC).

A.9.3 Synthetic procedures

A.9.3.1 Inimers synthesis

Four inimers as listed in Scheme B2 were synthesis according the reported procedures, based on esterification reactions between HEA/HEMA and α-bromoisoobutyryl bromide/2-bromopropanoyl bromide. The $^1$H NMR spectra with assignments of these four inimers are shown in Figure B1, confirming successful syntheses with purified compounds.

Inimer 1: $^1$H NMR (in CDCl$_3$, δ, ppm): 6.07 (1H, CH$_2$=C(CH$_3$)), 5.52 (1H, CH$_2$=CH), 4.35 (4H, OCH$_2$CH$_2$O), 1.88 (3H, CH$_2$=C(CH$_3$)), and 1.86 (6H, C(CH$_3$)$_2$Br).

Inimer 2: $^1$H NMR (in CDCl$_3$, δ, ppm): 6.51 (1H, CH$_2$=CH), 6.32 (1H, CH$_2$=CH), 5.98 (1H, CH$_2$=CH), 4.45 (5H, OCH$_2$CH$_2$O & CH(CH$_3$)Br), and 1.86 (3H, CH(CH$_3$) Br).
Inimer 3: $^1$H NMR (in CDCl$_3$, δ, ppm): 6.48 (1H, CH$_2$=CH), 6.22 (1H, CH$_2$=CH), 5.88 (1H, CH$_2$=CH), 4.45 (5H, OCH$_2$CH$_2$O), and 1.96 (6H, C(CH$_3$)$_2$Br).

Inimer 4: $^1$H NMR (in CDCl$_3$ as, δ, ppm): 6.07 (1H, CH$_2$=C(CH$_3$)), 5.52 (1H, CH$_2$=C(CH$_3$)), 4.35 (4H, OCH$_2$CH$_2$O), 1.88 ppm (3H, CH$_2$=C(CH$_3$)), and 1.86 (6H, C(CH$_3$)$_2$Br).

Scheme B 2: Structures of inimers.
A.9.3.2 Photo catalyst PH-PTZ synthesis

Photo catalyst PH-PTZ was synthesized according to literature\(^{62}\) with high purity (Figure B2). \(^1\)H NMR in CDCl\(_3\) assignments could be found in Figure B2.
A.9.3.3 Solution polymerization of inimers with photoinduced ATRP

Solution polymerization of inimer (1-4) was carried out with \([\text{inimer } 1]_0/[\text{PH-PTZ}]_0 = 50/1\) with DMF as solvent. A glass test tube (10mL) equipped with a magnetic stir bar was charged with inimer (inimer 1 0.278g, inimer 2 0.250g, inimer 3 0.264g, inimer 4 0.264g, 1 mmol), PH-PTZ (1 mol % C of inimer, 2.75 mg, 0.01 mmol) and dimethylformamide (DMF, 1 mL). The reaction mixture was then sealed by a rubber septum and rapped by aluminum foil to avoid light radiation and deoxygenated with N\(_2\) bubbling for 30 min. The test tube was then placed in center of the photo-reactor chamber equipped with eight 420 nm light tubes and built-in cooling fan. Samples were taken at timed intervals under flow of N\(_2\) for \(^1\)H NMR and DMF SEC measurements of vinyl conversions and polymer molecular weights.

iv) Polymerization of inimers using photo catalyzed ATRP in microemulsion
In a typical polymerization of inimer 1 with \([\text{inimer 1}]_0/[\text{PH-PTZ}]_0 = 100/1\), PH-PTZ was dissolved (2.75 mg, 0.01 mmol) into inimer 1 (0.28 g, 0.01 mol) and 0.1 ml DCM at room temperature (avoid any light by wrapping the test tube with aluminum foil). After evaporating DCM, the resulting solution was slowly added into 13 ml aqueous solution containing 1 g Brij 98 surfactant with magnetic stirring to form a thermodynamically stable microemulsion (36-40 °C, open to air when emulsifying). The transparent and colorless microemulsion was purged with nitrogen for 30 minutes before radiated in center of eight 420 nm light tubes while cooling with built-in cooling fan of the photo-reactor chamber to maintain ambient temperature. At timed intervals, samples were withdrawn via a syringe fitted with stainless steel needle under \(N_2\) flow for THF SEC and NMR measurements. After 2 hours, the reaction was stopped by exposure to air and quenched with THF. The microemulsion was destabilized and polymers were isolated by centrifugation. Finally, the polymers wad purified by precipitating into methanol three times.

A.10 Results and discussion

A.10.1 Solution polymeriation of inimer

Summary of the solution polymerization with \([\text{inimer 1}]_0/[\text{PH-PTZ}]_0 = 50/1\) with DMF as solvent under 420 nm light radiation:

As shown in Figure B3 and Figure B4, the polymerization was very successful with repeated “on-off” cycling of the reaction to light. Inimers with 2-bromopropanoic
initiating site (i.e., inimer 2 and inimer 3) could be polymerized faster in comparison with inimers with 2-bromo-2-methylpropanoic initiating site (i.e., inimer 1 and inimer 4).

Figure B 3: Polymerization of inimers using PH-PTZ with repeated “on-off” cycling of the reaction to light.
A.10.2 The application of metal-free ATRP of inimer1 in microemulsion

Microemulsion of metal free ATRP SCVP with inimer 1 and PH-PTZ was carried out with \([\text{inimer } 1]_0/\text{[PH-PTZ]}_0=50/1\). PH-PTZ was premixed with inimer 1 and emulsification was achieved in dark (Caution: hood light should be turned off and round bottom flask should be wrapped with aluminum foil before starting the reaction since the reaction occurs in the exposure to the hood light). According the SEC result (Figure...
B5), there was only one particle per latex since there were no small fractions observed. The molecular weight was determined by SEC with a multi-angle leaser light scattering detector (MALLS) by $M_n,\text{MALLS}=700k$ with PDI= 1.8. The degree of branching was also determined by Inverse gated decoupled $^{13}$C NMR (Figure B6) with a high DB = 0.34 based on the reported method.\textsuperscript{59}

![Figure B 5: SEC trace of the hyperbranched polymer synthesized with [inimer 1]$_0$/[PH-PTZ]$_0$=50/1 in microemulsion (blue line is RI detector and red line is from MALLs detector).]
A.11 Conclusions

AB* inimers with A as polymerizable methacrylate/acrylate group and B* as bromine group could be activated by excitation of photo redox catalyst PH-PTZ to allow a metal-free ATRP SCVP. The polymerization is compatible with both solution media and heterogeneous microemulsion media. Solution polymerization is generally slower than microemulsion polymerization probably due to the concentration effect, and inimers with 2-bromopropanoic initiating site (i.e., inimer 2 and inimer 3) could be polymerized.
faster in comparison with inimers with 2-bromo-2-methylpropanoic initiating site (i.e.,
inimer 1 and inimer 4). It is demonstrated that polymerization of inimers in
microemulsion helped achieve high molecular weight and low dispersity.

A.12 References

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