Narrative Progress Report
PRF# : 58014-DN17
Project Title: Development of Isotactic Controlled Radical Polymerization Using Rationally Designed Lewis Acids
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This proposal aims to develop a stereo-controlled living radical polymerization through which a broad range of monomers can be isotactically polymerized under highly accessible reaction conditions. This has been a long-standing challenge due to the inherent difficulty in controlling the stereochemistry of the planar configuration of the sp^2 hybridized carbon of the free radical. In our design, a nitroxide radical tethered with Lewis acid complex (Fig. 1a) will be used in the nitroxide-mediated polymerization (NMP). We hypothesized that the Lewis acid anchored on the nitroxide radical can be coordinated by the heteroatoms in the active chain end, and therefore a consistent conformation can be retained at the active chain end (Fig. 1b). In this mode, the monomer will be more easily unidirectionally incorporated into the polymer chain end to construct the *m* diads.

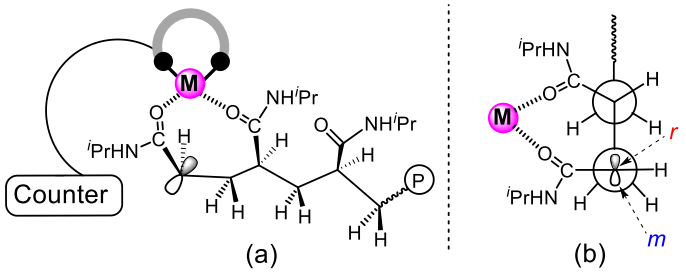

Fig. 1 The proposed mode for isotactic controlled radical polymerization assisted by Lewis acid.

Fig. 2a provided the proposed initiators based on 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO, **1**) that can enable a controlled NMP of various acrylate-based monomers. 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTAC, **2**) was designed to covalently link with TIPNO as a ligand. The coordination of TMTAC to the rare earth $Y(OTf)_3$ was confirmed by NMR analysis (Fig. 2c). Two chemical shifts in the ^1H NMR spectrum of TMTAC corresponds to the CH_2 and CH_3 in this molecule. Upon mixing with 1 equiv. $Y(OTf)_3$, TMTAC spectrum was split to three peaks with different chemical shifts, indicating coordination to Y, the two multi-peaks may be resulted from the autocoupling in CH_2. When 2 equiv. TMTAC was added to $Y(OTf)_3$, the peaks shifted again and may form a new structure.

There are three main steps in the synthesis of the precursor: (1) the synthesis of the hydroxyl functioned TIPNO. (2) The synthesis of TMTAC. (3) the linkage of the hydroxyl functioned TIPNO and the ligand. Currently, we have synthesized the hydroxyl functioned TIPNO **1** and TMTAC **2** successfully using the modified methods in the literature. We are still at the stage of searching an efficient route to obtain

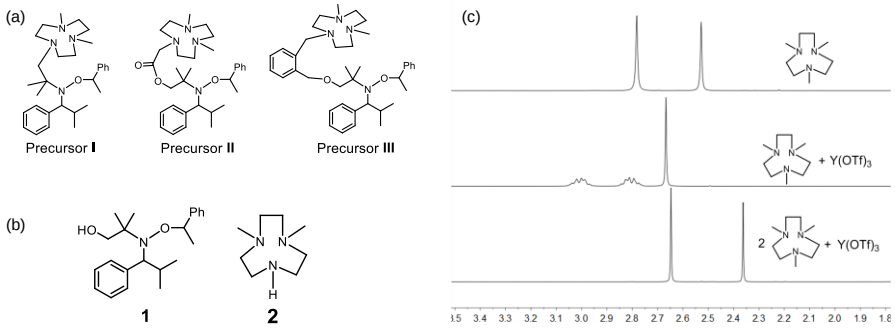

Fig. 2 (**a**) Proposed design of the precursors for isotactic controlled radical polymerization; (**b**) The initiator and ligand structure; (**c**) The ^1H NMR (left) and ^{19}F NMR (right) spectrum of 1,4,7-trimethyl-1,4,7-trizazcyclononane and its mixture with $Y(OTf)_3$

the proposed compound shown in Fig. 2a.

The postdoctoral researcher – Dr. Feng Li who was funded by the ACS PRF awarded – synthesized an interesting compound α-bromo butyl acrylate (αBBA) in one of the synthetic routes for the linkage of **1** and **2**. Dr. Li realized that this compound can be used as a novel polymerizable initiator in atom transfer radical polymerization (ATRP) to synthesize well-defined hyperbranched polymers (HPs). This work has been submitted for publication and is currently under review. Briefly, we demonstrated that copolymerization of αBBA and *n*-butyl acrylate (*n*BA) under ATRP conditions could result in site-specifically initiated HPs with controlled molecular weight (MW) and narrow distribution (*Đ* down to 1.15) (Fig. 3A). $M_{n,MALLS}$ – MW determined by GPC equipped with a multi-angle static light scattering detector – exhibits excellent agreement with the theoretical MW that was calculated according to the conversions of *n*BA and αBBA monitored by NMR (Fig. 3C). A spacing value X_n was defined as the average number of monomers inserted between two neighboring branching junctions to evaluate the degree of branching (DB), as the *n*BA comonomer does not contribute to the branched structure. ^{13}C nuclear magnetic resonance (NMR) spectra confirmed the branched structure (Fig. 3D and E). ^{13}C NMR provided X_n consistent with the results calculated from kinetic data. X_n in a broad range (X_n ~ 4– 43) was achieved by varying the feed rate and the stoichiometry of the *inibramer* and the comonomer. Well-defined HPs were prepared by copolymerizing with other comonomers, including methyl methacrylate (MMA), methyl acrylate (MA), styrene (St), acrylonitrile (AN), and *N*-isopropylacrylamide (NIPAAm). A polydimethylsiloxane (PDMS) macroinitiator was then used to initiate the copolymerization of αBBA and *n*BA (Fig. 3A). A clear shift of the GPC trace from the macroinitiator (Fig. 3F) suggested that a linear-*block*-hyperbranched architecture was synthesized. The absence of low MW polymers confirms that αBBA cannot be activated by Cu^I/L and that the HP is exclusively grafted from the PDMS chain end.

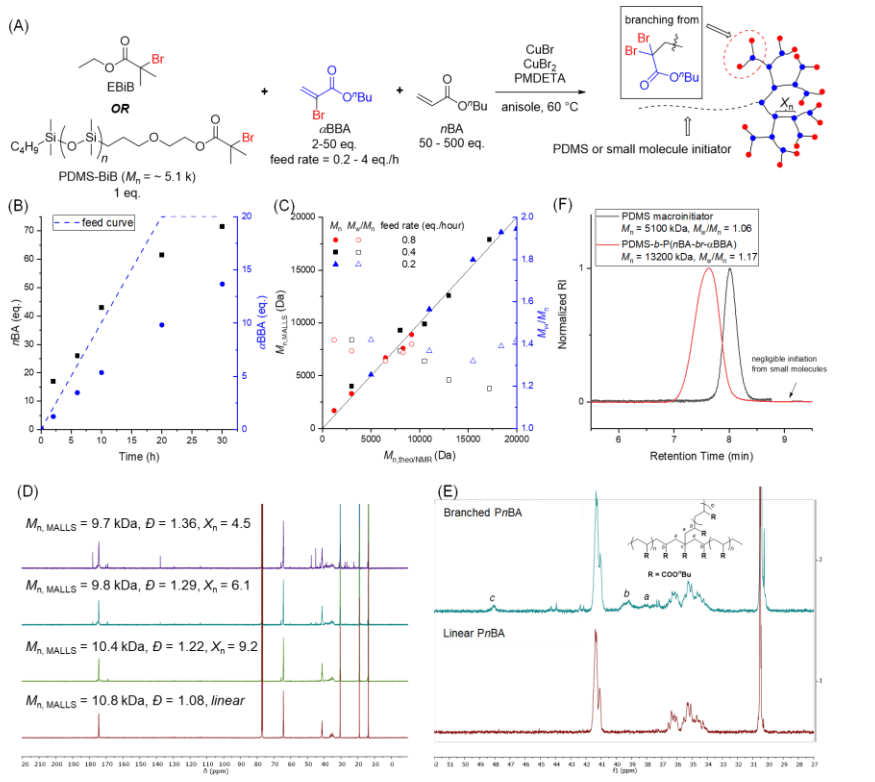

Fig. 3 (**A**) Synthetic route to site-specifically initiated HPs by ATRP of αBBA and *n*BA; (**B**) Kinetic plot for ATRP under conditions: [αBBA]/[*n*BA]/[EBiB]/[CuBr]/[$CuBr_2$]/[PMDETA] = 20/200/1/0.9/0.1/1 at 60 °C, feed rate of αBBA = 0.4 eq./hour; (**C**) Comparison of $M_{n,MALLS}$ with theoretical MW at various feed rates of αBBA; (**D**) Full ^{13}C NMR spectra for HPs with different MWs and X_ns; (**E**) NMR evidence for *inibramer*-derived branching structure; (**F**) GPC traces of chain-extension with branched P*n*BA from the linear PDMS macroinitiator.