

Catalytic Living ROMP: Synthesis of Degradable Star Polymers

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ABSTRACT: Star polymers have attracted considerable attention over the last years due to their distinctive physical and chemical attributes that are different from conventional linear polymers. Here, we present a one-pot synthesis of narrowly dispersed and degradable homo-arm and mikto-arm star polymers exploiting the catalytic living ring opening metathesis polymerization (ROMP) mechanism. Several complex polymeric architectures (such as A_3 , A_4 , A_6 , A_2B , A_3B , AB_2 type star polymers) were synthesized quite straightforwardly by using appropriate vinyl ether chain transfer agents. SEC, ^1H NMR, and DOSY NMR spectroscopy were employed to analyze and characterize all the synthesized polymers. We believe that this sustainable and environmentally friendly synthesis of star polymers could become an important synthetic tool for polymer engineers working on supramolecular, industrial or biomedical applications.

Introduction

Star polymers are complex macromolecular arrangements with at least three linear “arms” radiating from a central point, defined as the “core”.¹ They have attracted the interest of the polymer community over many years because of their distinct three-dimensional architecture with a diverse range of applications.^{2,3,4,5,6,7} Their compact structures, high functional group density, and unique properties make them promising tools for use in biomedical applications, drug delivery, nanotechnology, and other applications.^{8,9,10} We can categorize them broadly in two ways: first, as regular star polymers with identical arm segments, and second, as mikto-arm star polymers with two or more diverse arm compositions.^{1,11} Syntheses of these star polymers are mostly accomplished through living anionic polymerization, controlled/ living radical polymerization or ring opening metathesis polymerization (ROMP).^{12,13,14,15,16,17,18,19} Among them, high functional group tolerance, benign experimental conditions, vast monomer pool, facile end group modification and precise control over molecular weight have made ROMP highly prevalent and attractive in the polymer community.^{20,21,22} Over the previous decades, numerous endeavors have been undertaken to produce star-shaped ROMP polymers. In the 1990s, the Schrock group first demonstrated the synthesis of star polymers by ROMP via an “arm-first” approach method.²³ Various homopolymers, block copolymers and mikto-arm star polymers were synthesized by this approach. In 2007, Matyjaszewski reported the synthesis of mikto-arm star polymers by atom transfer radical polymerization using a simple and general “arm-first” method.²⁴ Later, Nomura and co-workers synthesized star shaped ROMP polymers via a “core first” approach.²⁵ In this method, a sequential ROMP of norbornene, cross-linker and, again, norbornene was performed to afford star polymers. In 2012, Johnson and co-workers developed the “brush-first” strategy to access star polymers via ROMP.²⁶ Numerous efforts were also undertaken to create star-shaped polymers using multi-armed

ruthenium catalysts, incorporating ROMP and click chemistry through a grafting-onto strategy, and developing trifunctionalized catalysts, including those from Hoveyda-Grubbs’ and Blechert’s catalyst.^{27,28,29,30}

Nevertheless, in all these scenarios, just like in traditional ROMP, a stoichiometric amount of ruthenium or molybdenum-based metal initiator is required with respect to the number of polymer chains formed. This frequently yields elevated catalyst quantities, entailing substantial costs and introducing hazardous impurities into the produced polymers, conceivably impeding the utilization of these substances in industrial and biomedical sectors.^{31,32}

Hence, there is an acute necessity to devise innovative methodologies to produce star-shaped ROMP polymers utilizing only catalytic traces of transition metal complexes. Recently our group has reported the synthesis of homo-arm star polymers using catalytic amounts of ruthenium initiator.³³ Nonetheless, since this approach depends on a kinetically regulated chain transfer mechanism, the resultant star polymers exhibit wide dispersities. Hence, the advent of a catalytic living polymerization method, capable of producing homo-arm and mikto-arm star polymers through ROMP, would constitute a valuable enhancement to the array of synthetic techniques accessible to polymer chemists. Herein, we report a one-pot synthesis of narrowly dispersed homo-arm and mikto-arm degradable star polymers using vinyl ethers as chain transfer agents under catalytic living ROMP conditions.

Numerous recent studies in the literature have explored metathesis-based copolymerization using 2,3-dihydrofuran (DHF) as a precursor for degradable polymers.^{34,35,36,37} Our group has recently developed a versatile method for the one-pot synthesis of living and degradable ROMP polymers. This is achieved through the copolymerization of 2,3-dihydrofuran (DHF) with various

norbornene derivatives, utilizing vinyl ethers as chain transfer agents within a catalytic living ROMP environment.³⁸ The sluggish ring-opening kinetics exhibited by norborneneimide derivatives when reacting with the propagating Ru Fischer-carbene represent a crucial attribute that promotes swift and specific substitution between the advancing Fischer-carbene and the vinyl ether of the chain transfer agent (CTA) under the specified conditions. As soon as all CTA molecules have been transferred to the polymer chain ends, the Fischer-carbene exchange between these terminal groups surpasses the monomer propagation rate. This exchange process is characterized by its degenerative, reversible, and regioselective nature. This intriguing phenomenon gives the appearance that all polymer chains are growing concurrently on a macroscopic scale. Consequently, this quasi-simultaneous advancement of all chains

enables the straightforward synthesis of copolymers within a single reaction vessel. Furthermore, this approach affords meticulous control over the molecular weight, dictated by the monomer/CTA ratio, and facilitates the attainment of narrow molecular weight distributions. (Figure 1A, 1B).³⁸

In this report, based on the aforementioned mechanism, we synthesized several complex polymeric architectures such as homo-arm and mikto-arm star polymers via developing appropriate chain transfer agents via core-first approach. Also, due to presence of an acid labile moiety (vinyl ethers), the metathesis arms could easily be degraded under mild acidic condition.^{39,40,41}

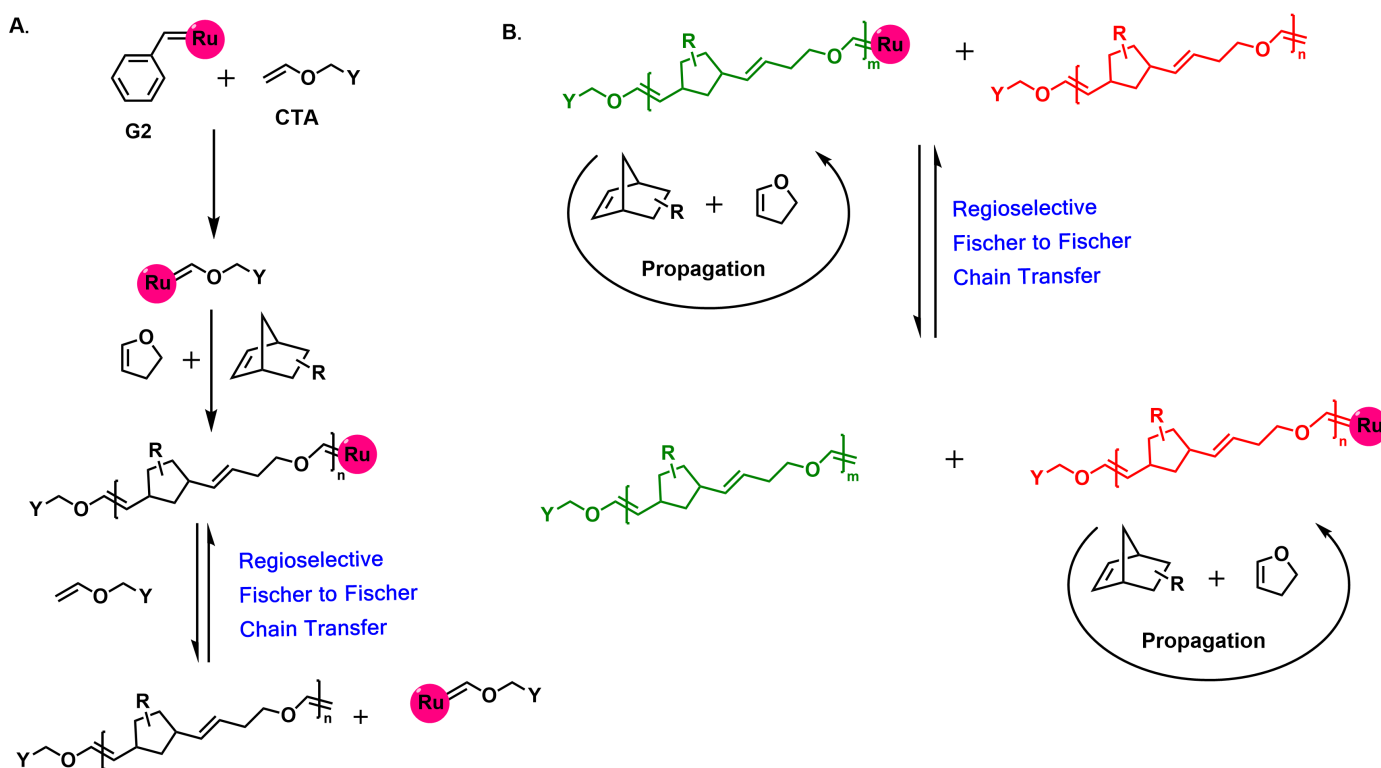


Figure 1.: A) Proposed general mechanism of catalytic living ROMP B) Mechanism of catalytic living ROMP illustrating reversible degenerative exchange between Fischer-carbene end groups.

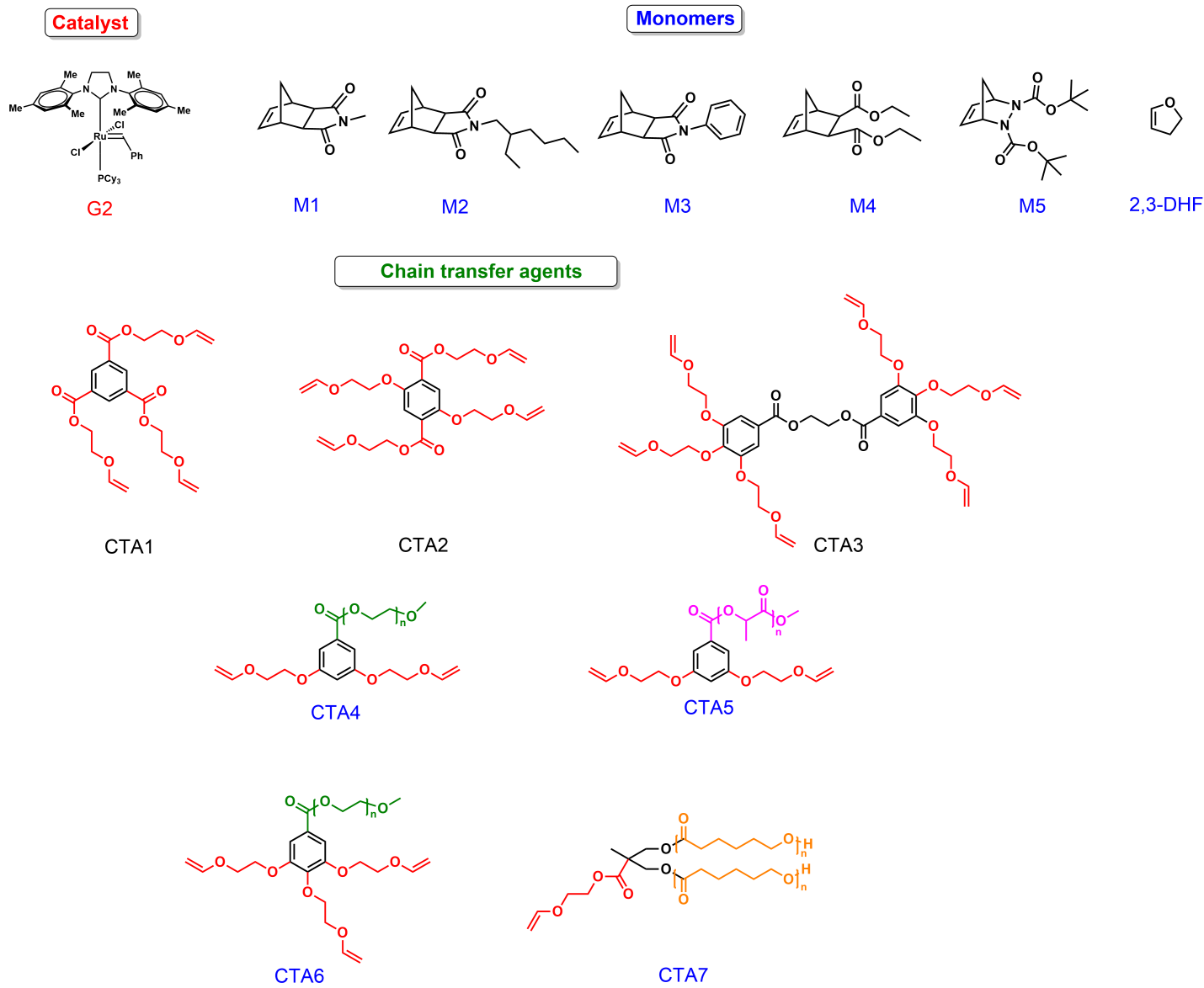


Figure 2.: Structures of the catalyst (G2), monomers (M1, M2, M3, M4, M5, 2,3-DHF), and chain transfer agents (CTA1-CTA7) used in this report.

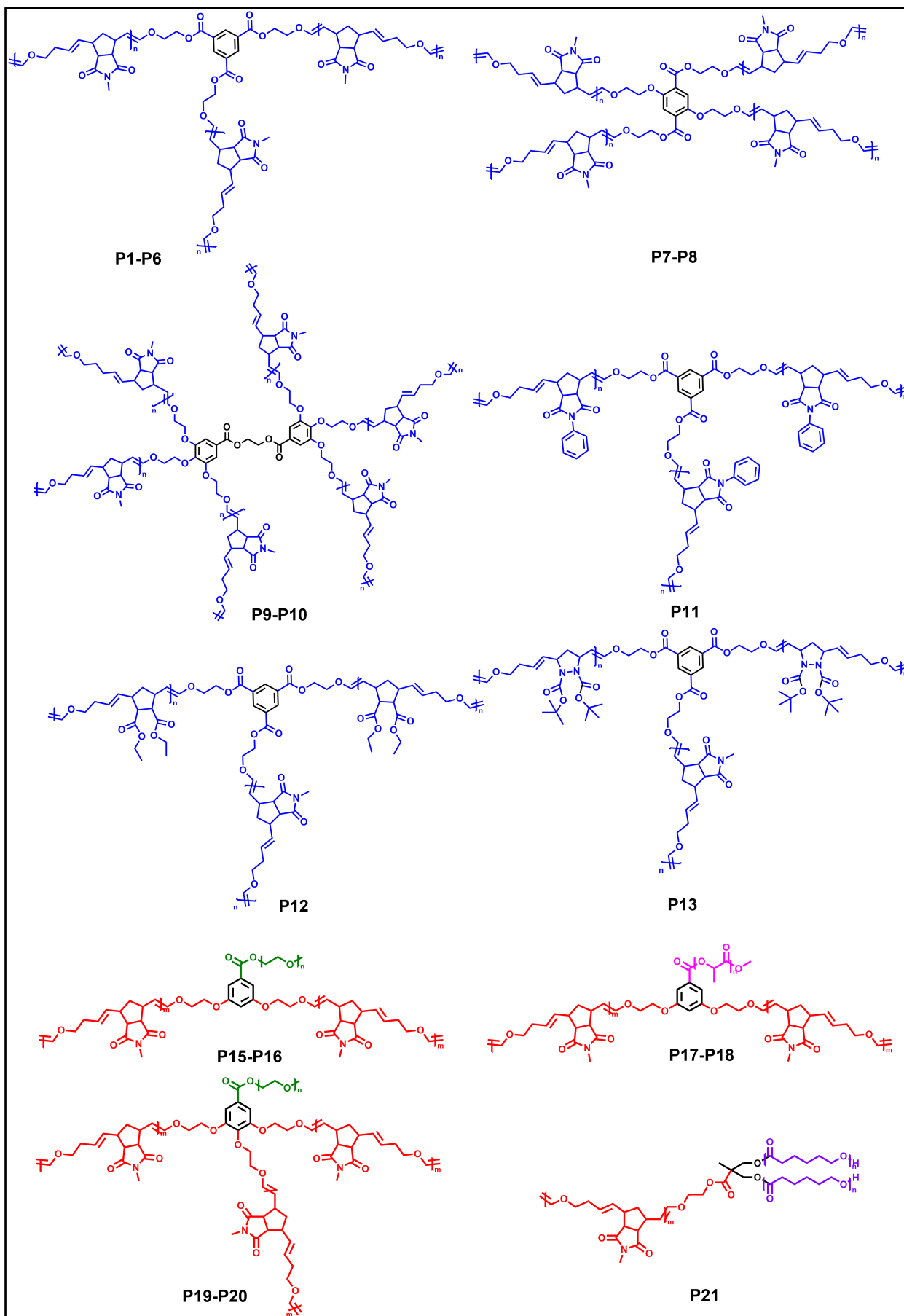


Figure 3.: Structures of the homo-arm (P1-P13) and mikto-arm (P15-P21) star polymers synthesized in this report.

Results and Discussion

We first synthesized trifunctional vinyl-ether based chain transfer agent **CTA1** (Figure 2). Then, a one-pot copolymerization using a ratio of **G2:CTA1:M1:DHF** of 1:10:180:360 was performed (SI, Table S1). ¹H NMR spectroscopy revealed full consumption of **CTA1** within the first 2 h of the polymerization, suggesting a trifunctional growth (SI, Fig S26). In addition, SEC analysis of the precipitated tri-arm star copolymer (after 24 h) showed a monomodal distribution with molar mass of 4.9 kDa (determined by **M1:CTA1** ratio) and a dispersity of 1.25 (SI, Fig S4).

Next, a series of tri-arm star copolymers (**P2-P6**) (Figure 3) were synthesized by varying the **M1:CTA1** ratio (using up to 100 times

less Ru complex than in a traditional ROMP polymerization). SEC and ¹H NMR spectroscopy were employed to analyze all the polymers. (SI, Table S1, entry 2-6, Fig S5-S9, Fig S49-S59). A linear correlation between molecular weight and the **M1:CTA1** ratio was observed as expected for a living copolymerization (Figure 4A). To further validate the living nature of the polymerization process, we prepared a block copolymer by dissolving polymer **P2** in DCM along with **M2**, **DHF**, and a catalytic quantity of **G2**. We confirmed the formation of a diblock copolymer, denoted as **P14**, through the noticeable shift of the SEC profile towards higher molecular mass (Figure 4B). Besides, DOSY NMR spectroscopy further confirmed the successful synthesis of the tri-arm diblock star copolymer (SI, Fig S78) showing a single diffusion species.

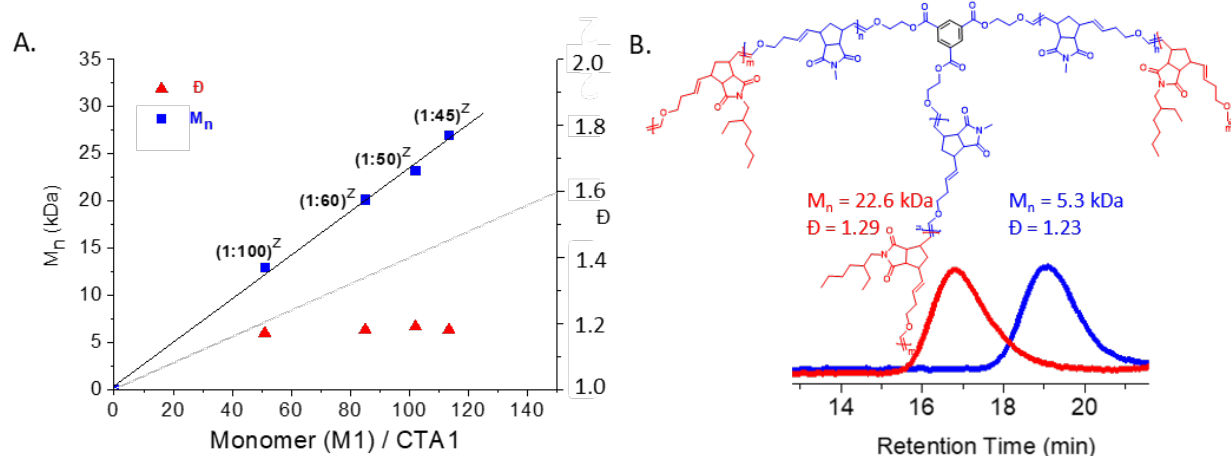


Figure 4.: (A.) Plot of the number average molar mass (M_n , SEC (CHCl₃)) and dispersity (D) versus $[M1]/[CTA1]$ ratio showing a linear correlation. The ratios reported in brackets (z) denote the $[G2]/[CTA1]$ ratio. (B.) SEC (CHCl₃) traces of the first block (tri-arm star copolymer **P2** (blue) and the tri-arm star diblock copolymer **P14** (red).

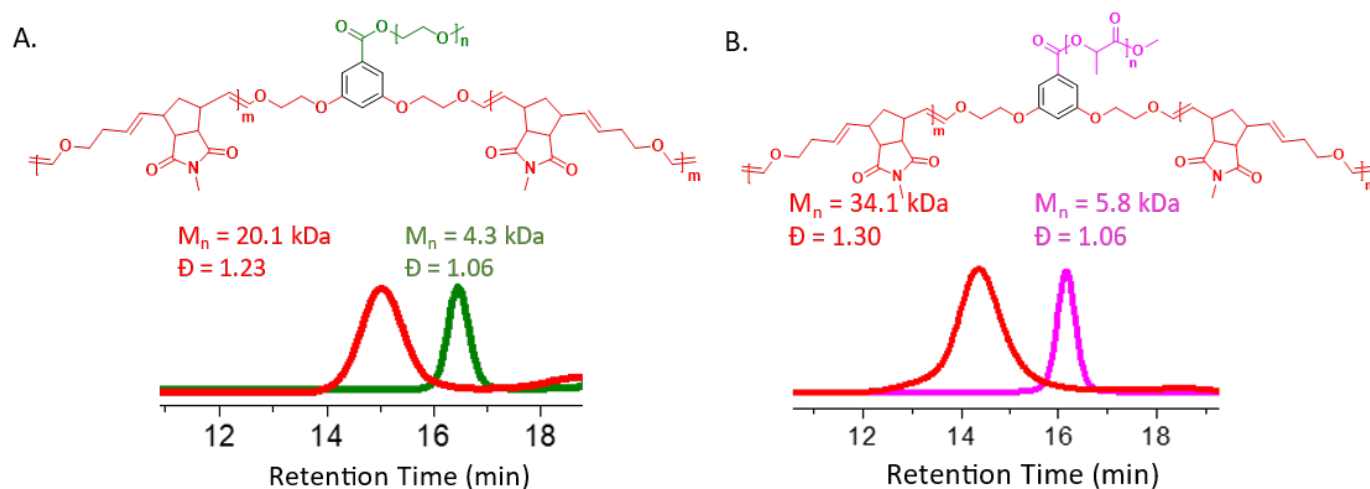


Figure 5.: (A.) SEC (DMF) traces of **CTA4** (green) and the mikto-arm star polymer **P15** (red). (B) SEC (DMF) traces of **CTA5** (magenta) and the mikto-arm star polymer **P17** (red).

A kinetic assessment further affirmed the living characteristics of the polymerization process. To investigate this, aliquots were taken

at various time points throughout the copolymerization of **M1** and **DHF** with **CTA1**, and subsequent analysis by SEC (SI, Table S3)

revealed a predictable, gradual rise in molar mass over time, consistent with the anticipated behavior of a living polymerization, characterized by consistently low dispersity (SI, Fig S2).

After that, we synthesized tetra-functional and hexa-functional chain transfer agents (**CTA2** and **CTA3**) in one straightforward step (Figure 2). Four-arm degradable star polymer **P7** and **P8** were synthesized, respectively, via copolymerizing **M1** and **DHF** using **CTA2** (SI, Table S1, entry 7-8). A combination of SEC and NMR spectroscopy confirmed the synthesis of the star-shaped copolymers (SI, Fig S10-S11, S60-S65). A one-pot copolymerization of **M1** and **DHF** using **CTA3** yielded the hexa-arm star polymers **P9** ($M_{n,SEC}$ (CHCl_3) = 14.81 kDa, \bar{D} = 1.34) and **P10** respectively (SI, Table S1, entry 9-10). The synthesized polymers were characterized by SEC and NMR spectroscopy (SI, Fig S12-S13, S66-S70). Next to demonstrate the versatility of this one-pot catalytic living copolymerization technique, we proceeded to copolymerize **DHF** with other monomers, namely **M3**, **M4**, and **M5** (as shown in Figure 2), while employing **CTA1**. This resulted in the synthesis of tri-arm star copolymers (**P11-P13**) with narrow dispersity, excellent monomer conversion, and precisely controlled molar mass (SI, Table S1, entry 11-13) To the best of our knowledge, this is the first report of synthesizing narrowly dispersed and degradable homo-arm star polymers as well as block copolymers using a catalytic amount of ruthenium complex in metathesis chemistry. Because of the existence of acid-sensitive vinyl ether motifs within the polymer structure,

exposing the hexa-arm star polymer **P10** to a mild HCl solution led to its total breakdown in just 30 minutes. (SI, Fig S25).

Next, we focused our attention on synthesizing more complex mikto-arm star polymers. **CTA4** was synthesized with polyethylene glycol (PEG_{4K}) as one arm and two vinyl ether units attached to two other arms of the core. One-pot copolymerization using a ratio of **G2:CTA1:M1:DHF** of 1:40:2800:5600 and 1:60:6000:12000 were performed to yield mikto-arm (A_2B type) star polymers **P15** and **P16** respectively where one arm consists of polyethylene glycol (PEG_{4K}) while the other two arms contain degradable metathesis polymeric units produced via catalytic living ROMP (SI, Table S2). The SEC analysis revealed the complete absence of the **CTA4** signal, concurrent with a significant increase in the molecular weight of the resulting mikto-arm star polymers. (Figure 5A and SI Fig S19). Additionally, DOSY NMR spectroscopy further supported the successful synthesis of the A_2B type star polymer (SI, Fig S81) as only a single diffusion species was observed. In a similar manner, **CTA5** was synthesized where polylactide was attached to one arm of the core. Mikto-arm star polymer **P17** and **P18** were synthesized via copolymerizing **M1** and **DHF** with **CTA5** under catalytic living ROMP condition (SI, Table S2). Confirmation of the successful synthesis of A_2B -type star polymer was evidenced by the presence of a sole diffusing species in the DOSY NMR spectrum and a noticeable shift in the SEC elugram in contrast to **CTA5**. (Figure 5B and SI Fig S21, Fig S85)

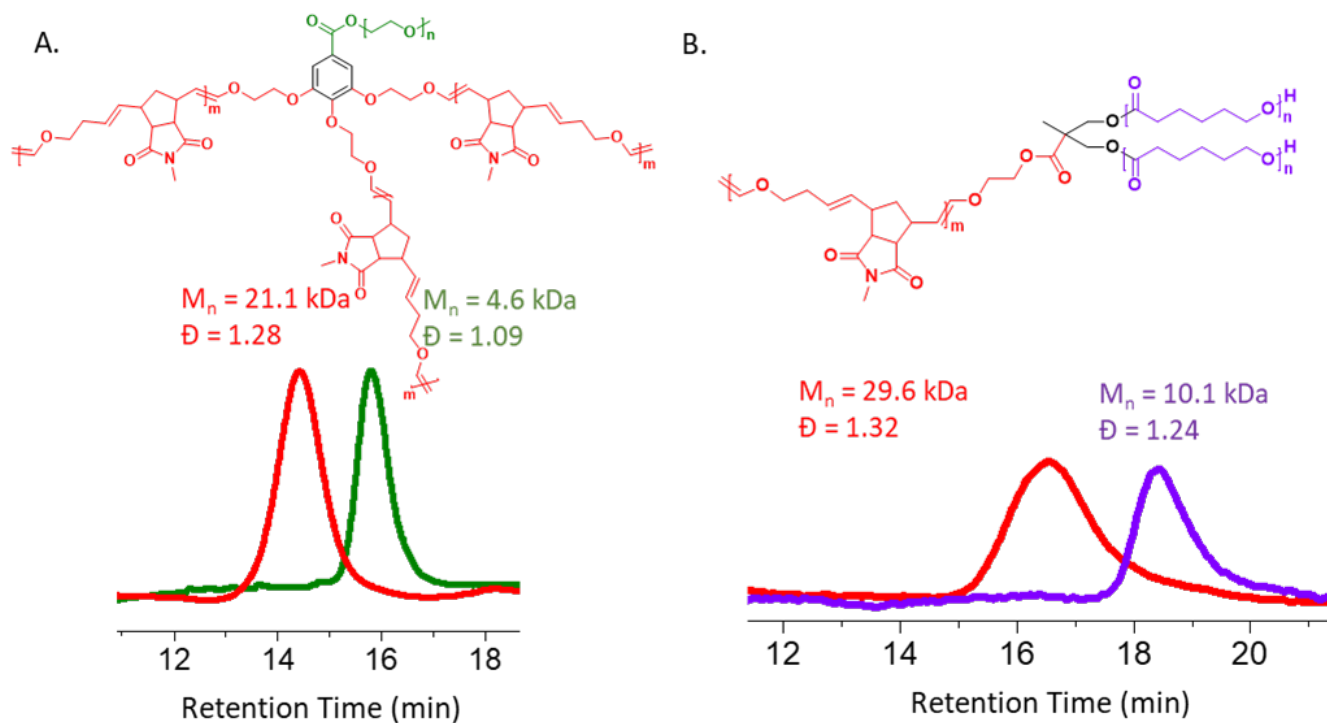


Figure 6.: (A.) SEC (DMF) traces of **CTA6** (green) and the mikto-arm star polymer **P19** (red). (B) SEC (CHCl_3) traces of **CTA7** (violet) and the mikto-arm star polymer **P21** (red).

After that, we synthesized **CTA6**, consisting of three vinyl ether moieties and one polyethylene glycol (PEG_{4K}) unit. Mikto-arm star polymers **P19** and **P20** containing three degradable metathesis arms and one PEG unit was synthesized in an analogous manner under catalytic living ROMP conditions (SI, Table S2). The synthesized

polymers (A₃B type) were characterized by SEC as well as DOSY NMR spectroscopy (Figure 6A and SI Fig S23, Fig S89).

Next, we synthesized **CTA7** comprising of one vinyl ether and two polycaprolactone units (synthesized via ring opening polymerization, see SI, Fig 24). A one pot copolymerization of **M1**, **DHF** and **CTA7** with catalytic amounts of **G2** yielded the AB₂ type star polymer **P21** (SI, Table S2). A clear shift in the SEC elugram ($M_{n,SEC}$ (CHCl₃) = 17.41 kDa, \bar{D} = 1.39) along with DOSY NMR spectra revealed the efficacious synthesis of the mikto-arm star polymer (Figure 6B and SI, Fig S93).

Conclusions

In conclusion, we have successfully designed a simple yet powerful strategy for the one-pot synthesis of metathesis-based narrowly dispersed homo-arm and mikto-arm star polymers using catalytic amounts of a Grubbs ruthenium catalyst. Different complex polymeric architectures (such as A₃, A₄, A₆, A₂B, A₃B, AB₂ type star polymers, with A being the metathesis block) were synthesized quite easily exploiting the regioselectivity and high metathesis activity of vinyl ethers as chain transfer agents. To the best of our knowledge, these types of macromolecular structures were synthesized for the very first time under catalytic living ROMP conditions. We believe this environmentally friendly (reduced use of ruthenium metal compared to conventional living ROMP) approach to synthesize different complex polymeric architectures will find many applications in bordering fields.

ASSOCIATED CONTENT

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Instruments data, Experimental methods, NMR data, SEC data. (PDF)

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Notes

The authors declare no competing financial interest.

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GRAPHICAL ABSTRACT

