Macro-chain Transfer Agents for Catalytic Ring-Opening Metathesis Polymerization

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ABSTRACT: A monosubstituted 1,3-diene derivative attached to a polymer is demonstrated to act as a macro-chain transfer agent in catalytic ring opening metathesis polymerization. PEG and PLA-based macro-chain transfer agents were synthesized in a few steps and were characterized using NMR spectroscopy, size exclusion chromatography (SEC) and matrix-assisted laser desorption/ionization-time of flight (MALDI-ToF) mass spectrometry. Poly(L-lactide) based diblock copolymer, poly(ethylene glycol) based diblock, and triblock (ABA type) copolymers of varied chain lengths were prepared catalytically in a one-pot approach via metathesis polymerization. Block copolymers were characterized by SEC and showed monomodal molecular weight distributions. Moreover, DOSY NMR spectroscopy further proved the block microstructures of the synthesized polymers.

Block copolymers (BCPs) have attracted considerable attention due to their ubiquitous applications in various fields such as emulsifiers, thermoplastic elastomers, adhesives, drug delivery, and many others over the last decades.[1,2,3,4] The synthetic approaches mainly include: (1) the sequential addition of monomers via living polymerization techniques. This method can yield BCPs with excellent control over molar mass and dispersity but is limited when the monomers are not suitable to be polymerized using the same mechanism. Another strategy is (2) coupling reactions of two active chain-ends of different polymer chains (such as the click reaction[5,6,7]). This technique often relies heavily on post-polymerization modifications of the polymer chain segments. Moreover, highly reactive, and orthogonal functionalities are required to avoid any homo-block after the coupling reaction.

On the other hand, very few techniques allow the use of polymeric chain transfer agents (macro chain transfer agents or mCTAs) to synthesize block copolymers. Among those, reversible addition-fragmentation chain transfer or RAFT polymerization involves chain transfer to a dithioester or trithiocarbonate-based CTA for the synthesis of well-defined block copolymers with an array of diverse functionalities.[8] Similar macro-CTAs were also used in a free radical chain transfer process to yield block copolymers in a straightforward approach.[9]

The advent of ring opening metathesis polymerization (ROMP) has allowed gaining access to functional block copolymers providing self-assembled nanostructures in solutions[10], applications in biology[11] , and materials[12,13]. Defined block copolymers of mainly norbornene imide-based monomers have been synthesized using functional group tolerant Grubbs catalysts[14] (Grubbs' 1st generation catalyst or **G1** and Grubbs' 3rd generation catalyst or **G3**) via adding monomers sequentially[15,16] or a one-pot approach[17,18,19]. In all the above cases, equimolar amounts of Grubbs' ruthenium complexes are generally required as the carbene complex was located at the end of each polymer chain. Our group recently reported a novel reversible chain transfer mechanism to synthesize ROMP block copolymers using catalytic amounts of metathesis catalysts.[20] Mechanistically this involves using a mCTA during the polymerization, however, so far, the monomers that have been explored to form block copolymers are only suitable to be polymerized using the same polymerization mechanism. In other words, only ROMP-ROMP block copolymers could be prepared via this methodology.[21] On the other hand ABA triblock copolymers were synthesized using the ROMP-ATRP or ROMP-RAFT approach, where the ROMP block (B part) was prepared using a symmetrical chain transfer agent,[22,23] thus employing a catalytic amount of ruthenium complex. Nonetheless, this approach is limited to a few sets of monomers (ROMP monomers that produce polymers with accessible double bonds capable of undergoing secondary metathesis reactions, such as cyclooctene, cyclopentene etc.), and due to mechanistic reasons, AB diblock copolymers cannot be prepared.

In this paper, we report a single-step, one-pot approach for the synthesis of poly(ethylene glycol) (PEG_{4k})-ROMP diblock, ROMP-PEG_{2k}-ROMP triblock, and poly(L-lactide) (PLA_{5k})-ROMP diblock copolymers using PEG, PLA based mCTAs and utilizing only catalytic amounts of expensive and toxic ruthenium based metathesis catalysts. We chose PEG as a hydrophilic chain segment due to its commercial availability, biological tolerance, and exciting self-assembly potential that has been studied extensively in the literature.[24,25,26,27,28] To the best of our knowledge, there is

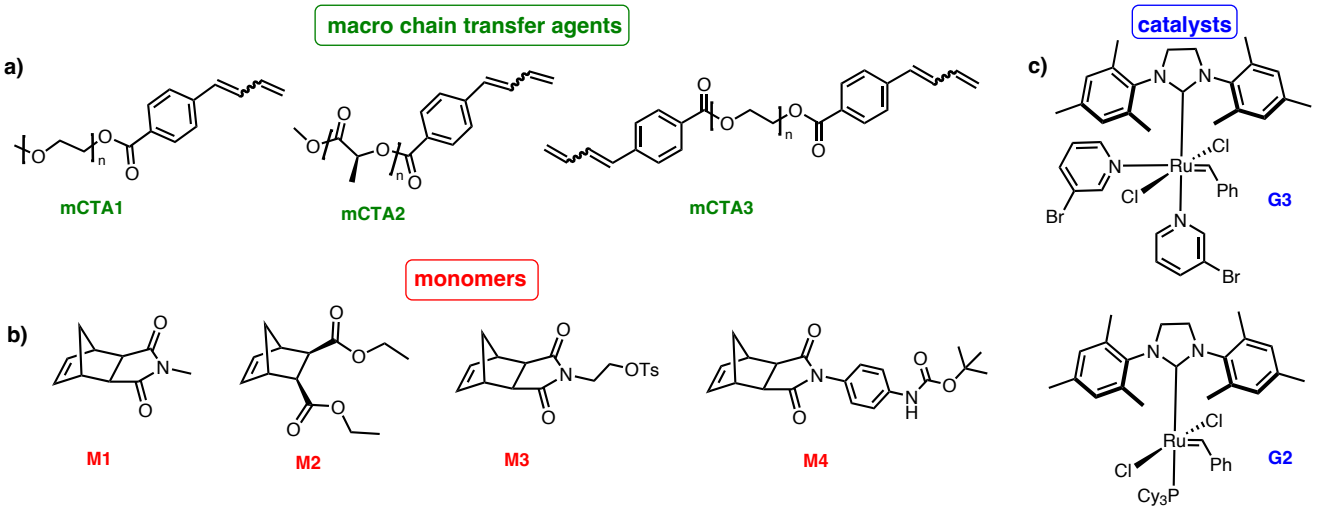

Figure 1. Chemical structures of the compounds studied here and synthetic route for macro-chain transfer agents (mCTAs). a) Structures for PEG and PLA based mCTAs. b) Structures of monomers. c) Structures of Grubbs' catalysts.

no report of PEG/PLA-based macro-CTAs (Figure 1a) for the synthesis of well-defined block copolymers in metathesis polymerization.

We have recently shown that monosubstituted 1,3-diene derivatives could be used as regioselective chain transfer agents to synthesize norbornene-imide-based ROMP polymers catalytically that involved a kinetically controlled chain transfer polymerization[29]. The very high reactivity of conjugated double bonds towards Grubbs' catalyst further allowed us to prepare block copolymers via macroinitiation from a PEG. We anticipated that if the 1,3-diene derivatives maintained the same chain transfer reactivity when attached to a polymer, they could be further employed to synthesize block copolymers catalytically using a similar kinetically controlled mechanism. Thus, PEG and PLA mCTAs were prepared through Steglich esterification between a 1,3-diene aromatic acid and alcohol functional monomethyl PEG_{4K} (**mCTA1**), PLA_{5k}(**mCTA2**), and PEG_{2K}(**mCTA3**). The 1,3-diene aromatic acid was synthesized via a two-step procedure: a Wittig olefination followed by an alkaline hydrolysis (see SI). These macro-CTAs were purified via simple precipitation from diethyl ether or methanol solution and further characterized using ^{1}H NMR spectroscopic and MALDI-ToF MS analyses which showed complete 1,3 diene functionality (see SI). Different degrees of chain extension with ROMP blocks from the macro-CTAs gave a series of diblock copolymers having different hydrophobic to hydrophilic volume ratios in the block composition, and the number average molar mass (M_n) of the final block copolymer was simply chosen by the monomer to mCTA ratio.

To begin with, **M1** was polymerized using **mCTA1** and **G3** in a ratio of **G3**: **mCTA1**: **M1** of 1:10:150. Complete consumption of monomer was confirmed by ^{1}H NMR spectroscopy. Then, a few drops of ethyl vinyl ether were added, and the resulting solution was precipitated into diethyl ether to obtain a white solid polymer **P1**. SEC analyses in DMF showed a molar mass increase slightly higher than determined by the **M1**/**mCTA1** ratio ($M_{n,\,SEC\,(DMF)}$ =10.2 kDa vs. $M_{n,\,theo.}$ =6.6 kDa) and a dispersity of 1.65. The observed M_n was a little bit higher as compared to the theoretical value. This may be attributed to the fact that SEC (DMF) was calibrated against the narrow disperse poly(ethylene glycol) calibrants which should have different hydrodynamic radius as compared to our polydisperse block copolymers. It must be noted that M_n determined from ^{1}H NMR end group analysis were very close to that of the theoretical molar mass of the diblock copolymers (see Fig. S1).

The addition of CTA (in the present case mCTA) to a polymerization system stops the propagating polymer chain by transferring the active species (Ru alkylidene complex) from the polymer to the CTA, thus starting another chain growth cycle (Figure 2). In other words, one molecule of initiator (Grubbs' catalyst) can produce several polymer chains (thus making the process catalytic), and consequently number average molar mass can be determined by monomer to CTA ratio, rather than the monomer to catalyst ratio which is commonly employed for a conventional ROMP. Moreover, to obtain complete control over molar mass of the polymers synthesized via this method, full consumption of the CTA is necessary. A catalytic ring opening metathesis polymerization that exploits a kinetically controlled chain transfer mechanism will depend on the relative rate of propagation of monomer and chain transfer to the CTA. Ideally, the rate of chain transfer to the CTA should be comparable to that of the propagation rate of the highly strained monomers to achieve a good control of the molar mass[29].

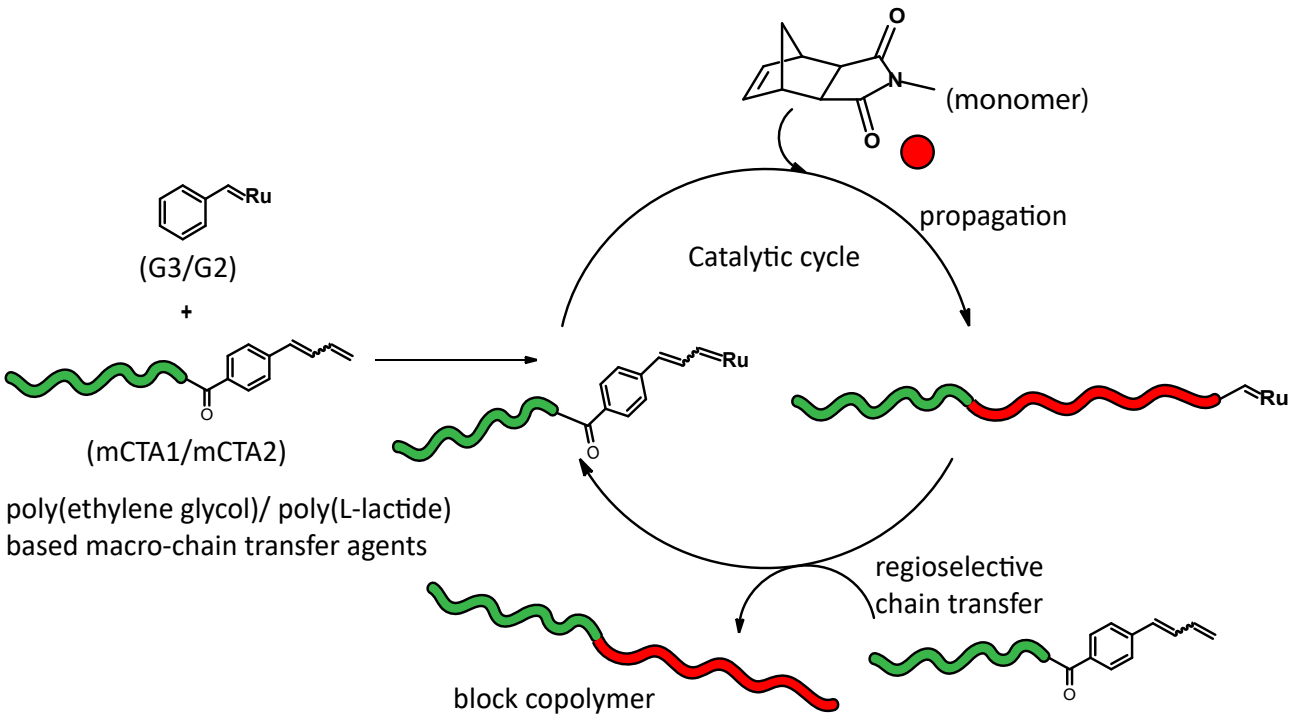

Figure 2. Mechanism for catalytic chain transfer metathesis polymerization for the synthesis of block copolymers using mCTAs. Macro-chain transfer agent reacts regioselectively with **G3**/**G2** to produce a conjugated carbene complex which reacts with monomer (**M1** is shown here) in the propagation step to form a propagating Ru alkylidene species. Due to high reactivity of our mCTAs, propagating metal complex is end capped irreversibly in a regioselective chain transfer step to give the conjugated metal complex back which concludes the catalytic cycle.

Furthermore, when the polymerization was performed varying the monomer to **mCTA1** ratio, a linear correlation for M_n vs. monomer/**mCTA1** was obtained (Figure 3), showing an excellent control of the chain extension of the diblock copolymers (for **P2** see Figure 4a and for **P3** see Fig. S43). Next, a cheaper and much more robust Grubbs' 2nd generation catalyst (**G2**) (Figure 1c) was employed under otherwise

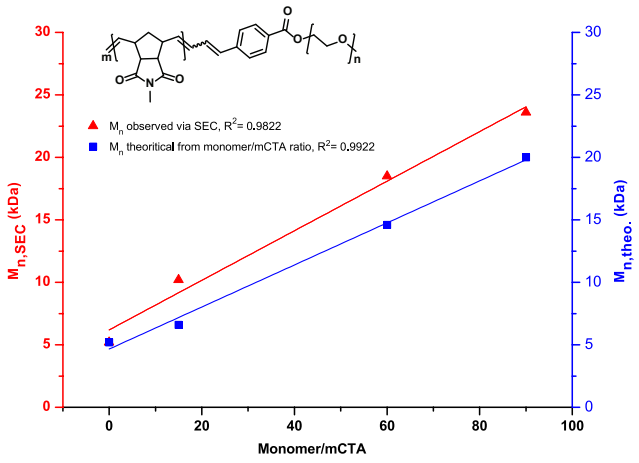

Figure 3. Linear dependency of observed M_n (SEC in DMF) vs. monomer to mCTA ratio and comparison with the theoretical M_n value.

similar polymerization conditions to obtain diblock copolymers **P4** (**G2**: **mCTA1:M1**= 1:40:3200, $M_{n,\,theo.}$ = 18.2 kDa , $M_{n,\,SEC\,(DMF)}$ = 24.3 kDa) and **P5** (**G2**: **mCTA1:M1**= 1:100:5000, $M_{n,\,theo.}$ = 12.9 kDa, $M_{n,\,SEC\,(DMF)}$ = 17.0 kDa) with complete consumption of monomer. SEC analyses of the precipitated polymers showed a monomodal distribution with a distinct shift towards shorter retention times in the SEC elugrams suggesting the formation of diblock copolymer (see Fig. S44 and Fig. S45 respectively). Moreover, a single diffusing species was observed in DOSY NMR spectroscopy (see Fig. S17 for **P4** and Fig. S20 for **P5**) which further confirmed the successful synthesis of diblock copolymers. It is worth mentioning that our methodology of chain extensions from a macro-CTA does not involve any further purification of the final diblock copolymers (other than simple precipitation into diethyl ether). Besides, monomodal distributions with no signal at the elution time of the unreacted mCTA were observed.[24] Moreover, the absence of any mCTA signal in the SEC elugram further corroborated the predicted high reactivity of our macro-chain transfer agents.

Next, diester functionalized monomer **M2** was polymerized with **G2** and **mCTA1** to obtain **P6** with excellent control over the molar mass (**G2**: **mCTA1:M1**= 1:40:4000, $M_{n,\,theo.}$ = 27.8 kDa, $M_{n,\,SEC\,(DMF)}$ = 27.0 kDa) (Figure 4b). DOSY NMR spectroscopy showed a single line in the spectrum (see Fig. S22), confirming formation of a block copolymer. To demonstrate the versatility of this method, another macro-CTA other than PEG was also utilized. PLA-based macro chain transfer agent, **mCTA2,** was employed to obtain **P7** (**G3**: **mCTA2:M1**= 1:50:3500, $M_{n,\,theo.}$ = 17.4 kDa, $M_{n,\,SEC\,(DMF)}$ = 22.0 kDa)(Figure 4c) and **P8** (**G2**:**mCTA2:M2**= 1:50:2500, $M_{n,\,theo.}$ =

17.4 kDa, $M_{n,\,SEC\,(DMF)}$ = 22.3 kDa) with a monomodal distribution and a clear shift of the SEC elugram from the first block to the diblock copolymer (see Fig. S46). Functional monomers such as **M3** (**P9**, **G3**:**mCTA1**:**M3**= 1:30:1200, $M_{n,\,theo.}$ = 18.4 kDa , $M_{n,\,SEC\,(DMF)}$ = 23.5 kDa)(Figure 4d) and **M4** (**P10**, **G2**:**mCTA2**:**M4**= 1:50:2500, $M_{n,\,theo.}$ = 22.7 kDa , $M_{n,\,SEC\,(DMF)}$ = 29.5 kDa)(Figure 4e) were also exploited in our catalytic system to synthesize diblock copolymers with controlled molar mass. We then focused our attention on synthesizing more complex block copolymers such as an ABA type, where the B part corresponds to a PEG unit, and chain extension (A) was achieved by ROMP. To prove chain extension from both sides of the mCTA, two controlled ^{1}H NMR experiments were performed. In the first experiment, 1 equiv. of the bifunctional PEG-macro CTA, **mCTA3** was reacted with 2 equiv. of **G3** and followed by ^{1}H NMR spectroscopy. The chain end protons (5.45 ppm and

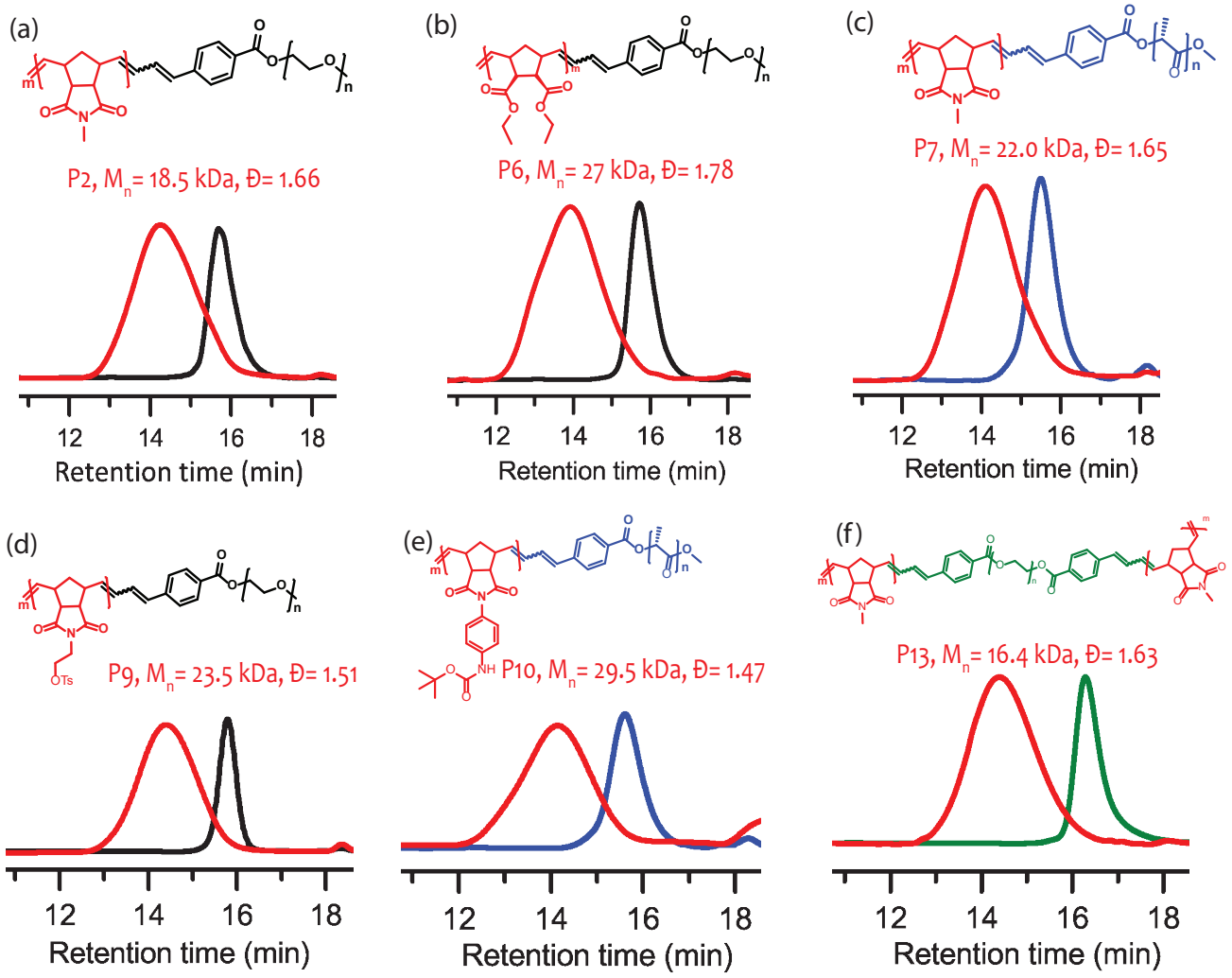

Figure 4. SEC analyses of the copolymers. (a) Diblock copolymer **P2** (red line) synthesized using **G3**: **mCTA1**:**M1**= 1:10:600. (b) Diblock copolymer **P6** (red line) synthesized using **G2**: **mCTA1: M2**= 1:40:4000. (c) Diblock copolymer **P7** (red line) synthesized using **G3**: **mCTA2**:**M1**= 1:50:3500. (d) Diblock copolymer **P9** (red line) synthesized using **G3**: **mCTA1**:**M3**= 1:30:1200. (e) Diblock copolymer **P10** (red line) synthesized using **G2**: **mCTA2**:**M4**= 1:50:2500. (f) Triblock copolymer **P13** (red line) synthesized using **G2**: **mCTA3**:**M1**= 1:200:14000. The black line (a, b, d) indicated the signal of **mCTA1** ($M_{n,\,SEC\,(DMF)}$ = 5.2 kDa, Đ= 1.12), the blue line (c, e) indicated the signal of **mCTA2** ($M_{n,\,SEC\,(DMF)}$ = 6.5 kDa, Đ= 1.17), and the green line (f) indicated the signal of **mCTA3** ($M_{n,\,SEC\,(DMF)}$ = 2.7 kDa, Đ= 1.20).

6.35 ppm) of **mCTA3** vanished entirely after adding 2 equiv. of **G3** and at the same time, the generation of 2 equiv. of styrene (5.75 ppm) was also observed (see Fig. S2). Therefore, attachment of the Ru complex on both sides of the **mCTA3** was achieved. In order to further confirm the chain transfer with the macro-CTA, we performed an NMR tube polymerization and monitored it by ^{1}H NMR spectroscopy. In an NMR tube, **M1** (3000 equiv.) and **mCTA3** (30 equiv.) were mixed in $CDCl_3$, and ^{1}H NMR was recorded. Then, 1 equiv. of **G2** was added to the same NMR tube. Complete consumption of **M1** (no triplet signal at 6.25 ppm) was observed over a period of 120 min, and simultaneously the chain end protons of **mCTA3** (5.2-5.4 ppm) shifted completely to the new chain end protons (5.1-5.2 ppm) of the tri-block copolymer, **P11** (see Fig. S3). This simple ^{1}H NMR experiment established the bi-functional chain transfer of **mCTA3**. At the same time, the consumption of both, monomer and macro-CTA throughout the polymerization verified the proposed kinetically controlled chain transfer mechanism[29]. SEC analysis of the resulting polymer showed

a shifted SEC trace compared with **mCTA3** (see Fig. S47). Following the same experimental procedures, **P12** (see Fig. S48) and **P13** (Figure 4f) were synthesized as triblock copolymers with control over molar mass and a monomodal signal in the SEC elugram. A kinetically controlled mechanism involves the irreversible chain transfer with the CTA and regeneration of the active species in each cycle. This process allows the predetermination of the average length of polymers synthesized but provides no means of dispersity control. This, in turn, reflected in the broader dispersities for the block copolymers.

In summary, metathesis-based hydrophilic-hydrophobic segmented PEG-b-P(M1/M2), P(M1)-b-PEG-P(M1) block copolymers and biodegradable poly(lactide) based PLA-b-P(M1) block copolymers were prepared via a new macro-chain transfer metathesis polymerization that utilized only catalytic amounts of transition metal catalyst. The macro-chain transfer agents were prepared in three straightforward steps and purified by simple precipitation. Catalytic polymerizations were performed using **G2**, a somewhat cheaper and bench stable alternative to **G3**. The catalyst to macro-CTA ratio was kept as low as 1 to 200, corresponding to a 200 times saving in costly and toxic ruthenium catalysts for the synthesis of the block copolymers. This novel methodology of using a macro-chain transfer agent to grow ROMP polymers is unique and could further be used to prepare different types of other block copolymers in a more cost-effective and greener way.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publication website. Instrument's data, Experimental methods, NMR data, MALDI-ToF data, and SEC data. (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

There are no financial conflict to declare.

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Graphical abstract: