Pulsed-Addition ROMP: Catalytic Syntheses of Heterotelechelic Polymers via Regioselective Chain Transfer Agents

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ABSTRACT: Regioselective chain transfer agents are used to synthesize narrowly dispersed heterotelechelic polymers with 15-fold decrease in catalyst consumption, using the pulsed addition ROMP (PA-ROMP) technique. Commercially available Grubbs' 3rd generation catalyst (**G3**) is easily prefunctionalized with the chain transfer agents in a short reaction time (30 min). After addition and consumption of a monomer, the excess chain transfer agent in the reaction medium end functionalizes the polymer chain and regenerates the initiator very quickly (within 10 minutes) via a ring-opening-ring-closing sequence. This regenerated catalyst then initiates the polymerization of a subsequent batch of monomer and the process is iterated for 15 times. Excellent control over molecular weight and dispersity from SEC analyses (over 15 pulses) confirmed the high efficacy of the chain transfer agents under this PA-ROMP method. The chain transfer agents are also extremely compatible with the synthesis of high molecular weight polymers (M/C = 150) with minimal catalyst decomposition. ^{1}H NMR as well as MALDI-ToF mass spectrometry further confirmed the high degree of chain end functionalization of the synthesized polymers.

Introduction

Ring opening metathesis polymerization (ROMP), which involves polymerization of strained cyclic olefin monomers, has evolved as a very important technique for polymer synthesis in a variety of disciplines such as material science, industry, medicine and academics.[1,2,3,4,5,6,7,8] Molybdenum-based complexes pioneered by Schrock and ruthenium-based complexes developed by Grubbs are the most predominant metathesis catalysts for synthesizing a variety of structurally and functionally diverse ROMP polymers.[9,10,11,12,13,14,15] Among all these, features such as commercial availability, high initiation/propagation rate ratio, functional group tolerance , mild reaction conditions and living polymerization have made Grubbs' 3rd generation catalyst (**G3**) most popular and widely used catalyst in ROMP for synthesizing different polymer architectures.[16,17,18,19,20,21]

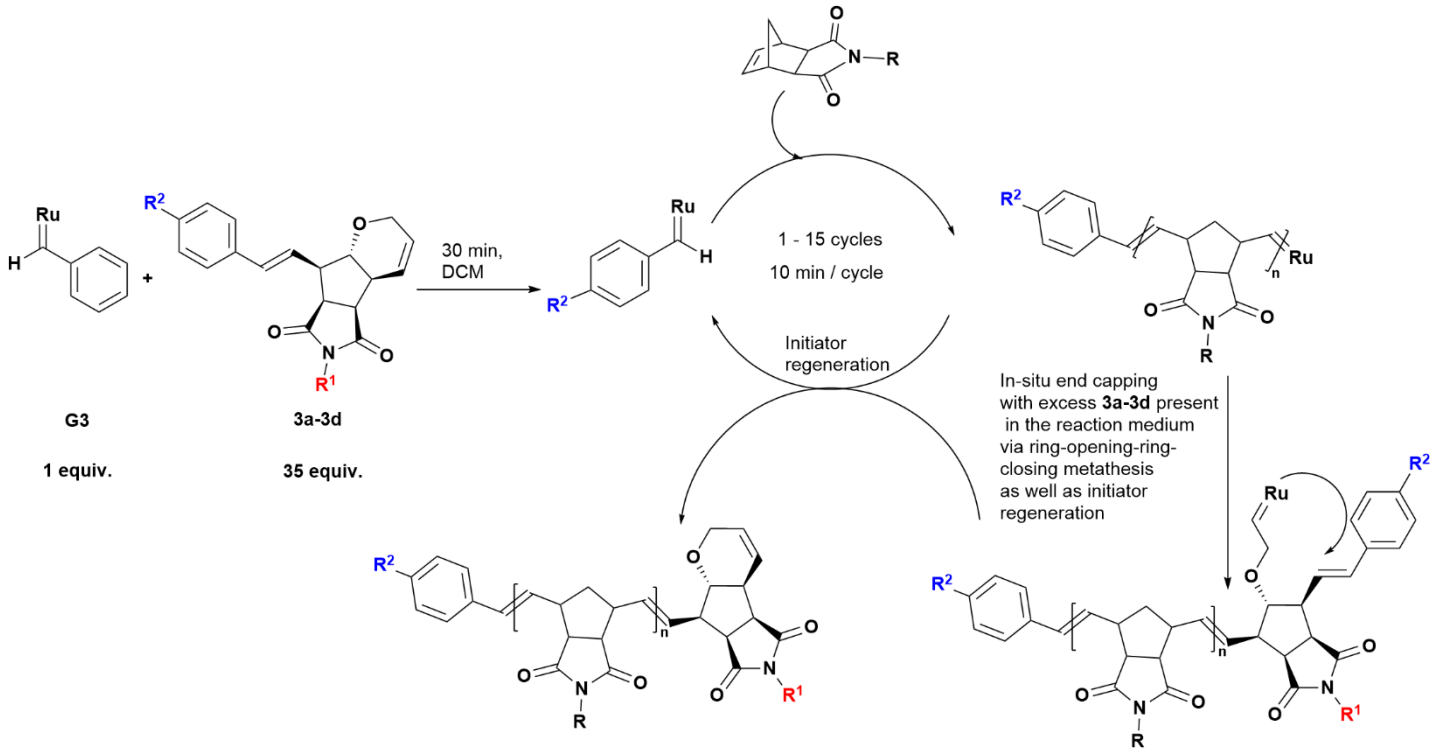
However, in a conventional living ROMP, a metal complex is always attached to end of the growing polymer chain. For this, a stoichiometric amount of ruthenium initiator is required with respect to the number of polymer chains formed. The requirement of using relatively large quantities of ruthenium complex leads to the potential high costs of polymer synthesis especially if short polymer chains are targeted. This also leads to high levels of ruthenium contamination in the synthesized polymers, which most of the time, are very difficult to remove. This high expense and difficultly in removing the residual toxic metal contaminants often makes the conventional living ROMP polymers unattractive in biomedical, electronic and industrial applications.[22,23] As a result, it has always been interesting and beneficial to develop new methods which reduce the amount of catalyst loadings for synthesizing well-defined ROMP polymers. However, to date, there are only few reports for preparing narrowly dispersed ROMP polymers using catalytic amounts of a ruthenium complex. Initially, several chain transfer agents (CTAs) were developed which were capable of exchanging the active metal species between different polymer chains, thus producing homotelechelic polymers by using sub-stoichiometric quantities of the metal complex.[24,25,26,27,28,29,30] However, these polymers are non-living showing broad dispersities due to significant and mechanistically necessary secondary metathesis. After that, several synthetic strategies have been developed to produce mono-telechelic, homotelechelic and heterotelechelic ROMP polymers with narrow dispersity and good molecular weight control, but all of these polymerization techniques require stoichiometric amounts of ruthenium initiators.[31,32,33,34,35,36,37,38,39,40] A heterotelechelic polymer synthesis using sub-stoichiometric amounts of catalyst has been reported by our group, however, polymers synthesized by this method show a broad dispersity for mechanistic reasons.[41] Recently, our group has reported reversible chain transfer agents (rCTAs) that exploit a degenerative reversible chain-transfer polymerization, resulting in living ROMP using only catalytic amounts of ruthenium complex.[42,43]

Another strategy of synthesizing polymers with sub-stoichiometric amounts of ruthenium initiator is pulsed-addition ROMP (PA-ROMP). Here, chain transfer agents (CTAs) are designed in such a way that the rate of propagation of the monomers is much faster than the rate of transfer to the CTAs. As a result, the monomers can be easily polymerized in the presence of excess CTAs. After consumption of the monomers, the living polymer chains are end-capped with the CTAs to regenerate the initiator. When another batch of monomer is added, new polymer chains are again formed, followed by end functionalization with the CTAs and catalyst regeneration. In this way, the cycle can be repeated multiple times. The pulsed addition ROMP was first reported by Schrock to prepare telechelic polymers using a molybdenum initiator.[44] Later, Gibson demonstrated this technique using ruthenium complexes.[45] In 2009, Matson and

Grubbs reported PA-ROMP up to ten cycles using Grubbs'3rd generation initiator, and *cis*-4-octene as the chain transfer agent.[46] However, this method is limited in synthesizing homotelechelic polymers only. Recently, Gutekunst has demonstrated the PA-ROMP technique up to 10 cycles with enyne-containing CTAs.[47]

Here, we report PA-ROMP up to 15 cycles to produce heterotelechelic polymers, with narrow dispersity and good molecular weight control, using regioselective chain transfer agents.

Scheme 1 : General strategy of pulsed addition ROMP (PA-ROMP) with CTAs 3a-3d



Results and discussion

Recently, while investigating new synthetic routes towards functional reversible chain transfer agents (rCTAs) for catalytic living ROMP,[42,43] we prepared several (see **Supporting Information Scheme S1**) functional CTAs (**3a,3b,3c,3d, Fig 1**).[40,48] However, initial kinetic studies revealed that the chain transfer constants of these new CTAs were too low[40] compared to their non-functional analogous compound (*E*)-7-styryl-2,4a,5,6,7,7a-hexahydrocyclopenta[b]pyran.[42] As the rate of propagation of the monomers (**M1**/**M2**) is much higher than the rate of transfer to these new CTAs, even a very slow addition of the monomers yielded polymers with broader dispersities.[40] However, in spite of these difficulties, these new functional CTAs are very useful for the preparation of one -pot heterotelechelic polymer synthesis.[40]

We already showed in our previous studies that due to the steric hindrance of the exocyclic double bond of this type of CTA, it reacts with the ruthenium complexes via its endocyclic double bond first in a ring-opening-ring-closing sequence.[42] Recently, we reported that, commercially available Grubbs' 3rd generation catalyst (1 equiv.) can be functionalized *in situ* (within 1 h) using excess of these new functional CTAs (20 equiv.).[40] As the rate of transfer to the CTAs is much slower than the rate of propagation of a norbornene derivative, subsequent polymerization of a norbornene derivative proceeds in presence of the excess CTAs. Finally, when all monomers have been consumed an automatic end functionalization (within 10 min) with the excess of the CTAs present in the reaction medium (via ring-opening-ring-closing-metathesis) yielded narrowly dispersed heterotelechelic polymers.[40]

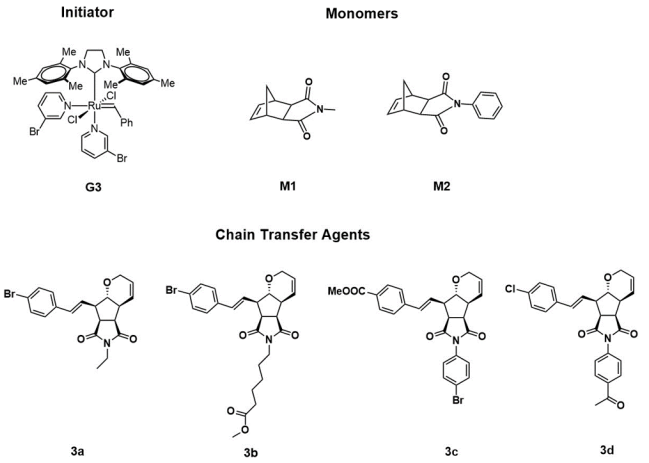


Fig 1: Initiator, monomers and chain transfer agents used in PA-ROMP reaction

After end-capping the polymer chain successfully, these CTAs regenerate the functional benzylidene initiator within 5-10 min. We, therefore, expected that they might be useful for pulsed-addition ROMP (PA-ROMP) to synthesize narrowly dispersed heterotelechelic polymers with sub stoichiometric amounts of Grubbs initiator. As the chain transfer rate of the CTA is much lower than the rate of propagation of the monomers, polymerization will take place in an uninterrupted way in the presence of excess CTA. When monomer consumption is complete, an *in-situ* end functionalization with the excess CTA present in the reaction medium (via a ring-opening-ring-closing-sequence) regenerate the initiator which can again polymerize a subsequent batch of monomer and the process can be iterated multiple times. Furthermore, there is no need to add additional CTA after each monomer pulse as an excess can be used from the start. (**Scheme 1**)

To prove the competence of these CTAs (**3a**,**3b**,**3c**,**3d**) in pulsed-addition ROMP, **G3** was reacted with 35 equiv. of CTA **3a**, and the reaction was followed by ^{1}H NMR spectroscopy. Within 25 minutes almost complete conversion(98%) of **G3** benzylidene (19.07 ppm) to **G3-Br** benzylidene (19.03 ppm) was observed (see **Supporting Information Fig S1a**). Consistent with our previous studies, when 20 equiv. of monomer **M1** was added, polymerization followed by regeneration of **G3-Br** benzylidene was observed within 5 minutes. After that, to check the efficiency of this process in multiple cycles, G**3** was first prefunctionalized with CTA **3a** under Schlenk conditions in a similar manner as described above. Then, 20 equiv. of monomer **M1** was added. After 5- 7 minutes (i.e., complete polymerization of the monomer followed by an in-situ end functionalization with excess CTA **3a** present in the reaction medium and new initiator generation), a small amount of sample was removed, quenched with ethyl vinyl ether and analysed by SEC. Then, another 20 equiv. of **M1** was added to the above solution and the aforesaid steps were repeated for 15 cycles. A narrowly dispersed polymer **P1** was obtained at the end of the 15 pulses. Analysis of each pulse by SEC displayed a monomodal distribution with low dispersity and controlled molecular weight over 15 cycles (**Fig 2**). The molecular weight slowly increases from 4119 Da to 5645 Da as the number of pulses increases from 1 to 15 (**Fig 3** , **Table 1** , **entry 1** , also see **Supporting Information Table S1**). (The molecular weight data obtained in each cycle is cumulative , i.e. , including previous cycles).

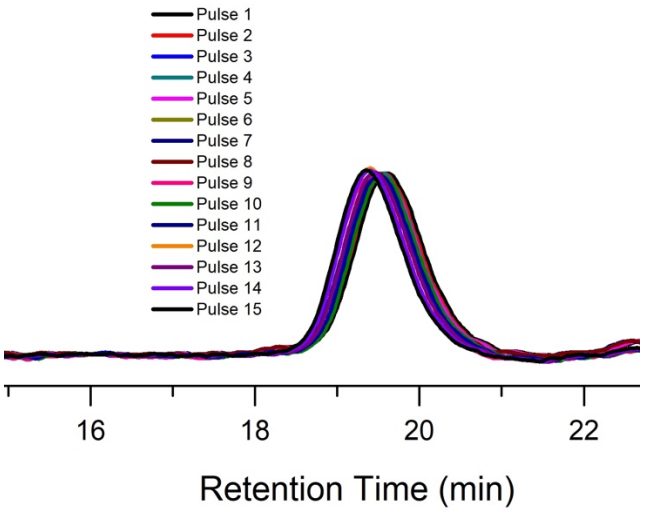


Fig 2: SEC ($CHCl_3$) traces of polymer **P1** over PA-ROMP cycles

This is presumed to be the result of slow catalyst decomposition after each cycle. Also, this pulsed technique was executed manually and samples were collected after each cycle for SEC analysis. It is conceivable less catalyst decomposition and thus better results might be obtained if an automated robot system is used as shown by Grubbs. The end groups of polymer **P1** were confirmed by MALDI-ToF MS as well as ^{1}H NMR spectroscopy (see **Fig 4** and **Supporting Information Fig S39**). The inset of **Fig 4** corresponds to an isotopically resolved MALDI-ToF mass spectrum matching the two expected end groups of polymer **P1**. Also, a repeating unit with an average of 177.03 g mol^{-1} confirms the correct molecular mass of monomer **M1.**

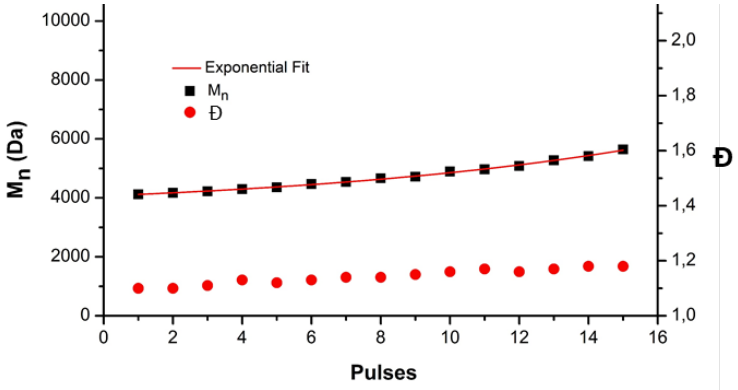


Fig 3 : Dependence of M_n and dispersity on number of PA-ROMP cycles of polymer **P1**

After the successful proof-of-concept, next we prefunctionalized **G3** with CTA **3b** (see **Supporting Information Fig S1b**). Upon generation of **G3-Br** benzylidene, additions of 10 equiv. of monomer **M1** were cycled for 15 times with a reaction time of 5-7 min for each cycle. At the end of the 15 pulses heterotelechelic polymer **P2** was obtained carrying a bromo phenyl moiety at one end and an ester group on the other end. The SEC analysis (see **Supporting Information Fig S9**) of each pulse showed a very slow increase of molecular weight from 2331 Da to 3489 Da over 15 cycles (**Table 1** , entry 2 , also see **Supporting Information Table S2 and Fig S3**). End groups were confirmed by both ^{1}H NMR as well as MALDI-ToF mass spectrometry (see **Supporting Information Fig S41 , Fig S52).**

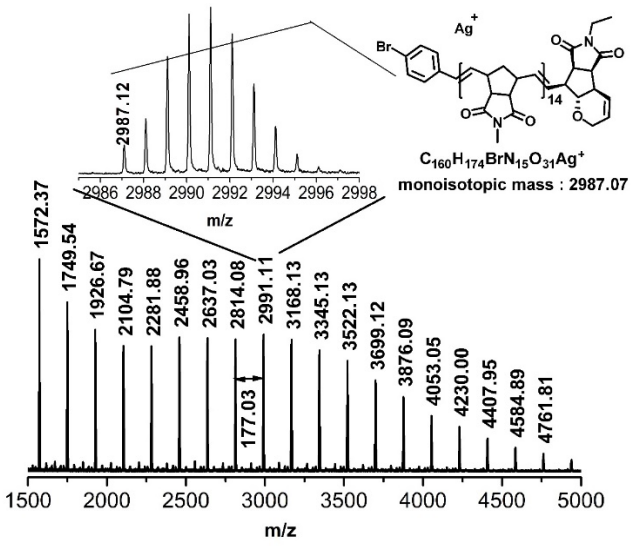


Fig 4: MALDI-ToF mass spectrum (DCTB, AgTFA) of polymer **P1** after 15 cycles

Next, to test the potential of PA-ROMP in synthesizing high molecular weight heterotelechelic polymers, **G3** was prefunctionalized with CTA **3b** in a similar manner as described above followed by addition of 50 equiv. and 150 equiv. of monomer **M1** respectively in each cycle. Heterotelechelic polymers **P3** and **P4** were obtained with good control over molecular weight and dispersity (**Table 1**, entry 4 and entry 5). The monomodal distribution with narrow dispersities and controlled molecular weights over all the pulses for both the polymer **P3** and **P4** confirmed the high efficiency of these chain transfer agents in the PA-ROMP technique (see **Supporting Information Table S3,S4 and Fig S4,S5,S10,S11**). Furthermore, analysis of the molecular weights obtained from each pulse for a very high ratio of monomer to catalyst (M/C = 150) (polymer **P4**) showed that only 25.8 % of catalyst decomposed after 15 cycles (see **Supporting Information Table S8).**This is a very significant improvement over previous reports where 80.3% of the catalyst decomposed over 10 cycles for a monomer to catalyst ratio of 100.[46] This clearly demonstrates that our new CTAs can not only be used to synthesize low molecular weights polymers as reported previously,[46,47] they can also be very effective in synthesizing high molecular weight heterotelechelic polymers with minimal catalyst decomposition.

Thereafter, another monomer structure was investigated to expand the efficacy of this method. Heterotelechelic polymer **P5** was synthesized by prefunctionalizing **G3** with CTA **3b** followed by subsequent addition of 10 equiv. of monomer **M2** over 15 cycles. The SEC traces (see **Supporting Information Fig S12**) of all the pulses showed the formation of narrowly distributed polymers with slow increase of molecular weight (3216 Da to 4698 Da) over the sequence (**Table 1** , entry 5 , also see **Supporting Information Table S5 and Fig S6)**. Also, ^{1}H NMR spectroscopy and MALDI-ToF mass spectrometric analyses confirmed the presence of the expected end groups. (see **Supporting Information Fig S46 , Fig S53)**

After that , to show the versatility of this method , different functional CTAs (**3c , 3d**) were synthesized. Then , in a similar fashion as described above , **G3** was prefunctionalized with CTA **3c** to generate the new carbene complex **G3-COOMe** (19.46 ppm) within a short reaction time (see **Supporting Information Fig S1c**). Thereupon , addition of 12 equiv. of monomer **M1** over 15 cycles gave a methyl benzoate initiated heterotelechelic polymer **P6** with a bromo phenyl moiety at the other chain end. The SEC analysis (see **Supporting Information Fig S13)**of each pulse showed a very slow increase of molecular weight (3012 Da to 4345 Da) over the entire process with narrow dispersities.(**Table 1** , entry 6 , also see **Supporting Information Table S6 and Fig S7**). Furthermore, the end groups of the polymer were analysed by both ^{1}H NMR as well as MALDI-ToF mass spectrometry (see **Supporting Information Fig S48 , Fig S54).**

Thereafter , in an analogous manner , heterotelechelic polymer **P7** carrying chloro phenyl group on one end and acetophenone moiety on the other was synthesized via prefunctionalization of G3 with CTA **3d** (see **Supporting Information Fig S1d**) followed by addition of 10 equiv. of monomer **M1** over 15 cycles . The SEC measurements displayed controlled molecular weight (2036 Da to 3088 Da) with low dispersity for all the pulses . **Table 1** , entry 7 , also see **Supporting Information Table S7 and Fig S8, Fig S14**). Also , ^{1}H NMR and MALDI-ToF mass spectrometry confirmed the high chain end fidelity of the synthesized polymer. (see **Supporting Information Fig S50 , Fig S55).**

Table 1 : PA-ROMP data

Entry	CTA	Monomer	G3:Monomer in each pulse	Polymer	Pulse	M_n (Obs) (Da) (SEC[a] $CHCl_3$)	Dispersity
1	3a	M1	20	P1	1	4119	1.10
					15	5645	1.18
2	3b	M1	10	P2	1	2331	1.12
					15	3489	1.17
3	3b	M1	50	P3	1	10013	1.09
					15	13813	1.21
4	3b	M1	150	P4	1	28123	1.08
					15	32910	1.16
5	3b	M2	10	P5	1	3216	1.11
					15	4698	1.17
6	3c	M1	12	P6	1	3012	1.09
					15	4345	1.15
7	3d	M1	10	P7	1	2036	1.10
						3088	1.15

[a]SEC ($CHCl_3$) was calibrated with polystyrene standards

Conclusions

In conclusion, narrowly dispersed heterotelechelic ROMP polymers (**P1**-**P7**) with 15-fold decrease in catalyst requirements were synthesized for the first time using single regioselective chain transfer agents using the PA-ROMP technique. As the reactivity of the monomer is much greater than these functional CTAs, polymerization followed by an *in-situ* end functionalization (via ring-opening-ring-closing-sequence) and initiator regeneration takes place very effectively making this method very attractive for synthesizing narrowly dispersed heterotelechelic polymers. These CTAs are also very efficient in producing high molecular weight polymers (M/C = 150) with minimal loss of catalyst activity. Also, the process does not require addition of CTA after each cycle. This shows that our method is very suitable for synthesizing different heterotelechelic polymers with a variety of norbornene derivatives. . Furthermore , different functional groups that can be addressed orthogonally to the backbone functional groups can be incorporated according to the particular needs. Some of these functional groups are shown in this report , such as , ester , ketone or halide. All of these can be further modified easily and their installation on the chain ends requires only a single chain transfer agent. In all cases, SEC analyses displayed a monomodal distribution with low dispersity and controlled molecular weight over 15 cycles. This supports the high efficacy of these regioselective chain transfer agents for producing heterotelechelic polymers with substoichiometric amounts of catalyst under the PA-ROMP technique. For polymers **P1, P2 , P5 , P6** and **P7** MALDI-ToF mass spectrometry confirmed the presence of both functional end groups. Overall, this method represents a catalyst economical and environmentally friendly synthesis of heterotelechelic polymers with low dispersity using single chain transfer agents. We believe that decreased metal contamination as well as reduced cost can make this technique very valuable , for example, in biomedical applications.

Experimental Section

A General Procedure for Pulsed Addition ROMP (PA-ROMP)

CTA **3a**/**3b**/**3c**/**3d** (35 equiv.) was taken in a Schlenk flask under argon, then dry degassed dichloromethane was added to it followed by addition of **G3** (1 equiv.) which was also separately dissolved in dry degassed dichloromethane (0.5 mL). The reaction mixture was stirred at room temperature for 30 min in order to ensure almost complete conversion of G3 to respective functional catalyst. After that a degassed solution of monomer (**M1**/ **M2**) (10 equiv. / 12 equiv. /20 equiv. / 50 equiv. / 150 equiv.) in dry dichloromethane (0.2 M) was quickly added to above solution. After 5-7 min, (i.e., complete polymerization followed by end functionalization and initiator regeneration) a small amount of sample was taken out, terminated with ethyl vinyl ether and analysed in SEC. Then again in a similar way, a degassed solution of monomer (**M1**/ **M2**) (10 equiv. / 20 equiv. / 50 equiv. / 150 equiv.) in dry dichloromethane (0.2 M) was quickly added to above solution and after 5-7 min, a small amount of sample was taken for SEC measurement. The steps were repeated for 15 cycles. At the end, the reaction mixture was quenched by adding ethyl vinyl ether and the solvent was removed under reduced pressure. The concentrated solution obtained was precipitated 3 times into cold methanol to give the respective heterotelechelic polymer (**P1**-**P7**).

ASSOCIATED CONTENT

Supporting Information

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

Instruments data, Experimental methods, NMR data, MALDI-ToF data, SEC data. (PDF)

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Notes

The authors declare no competing financial interest.

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GRAPHICAL ABSTRACT