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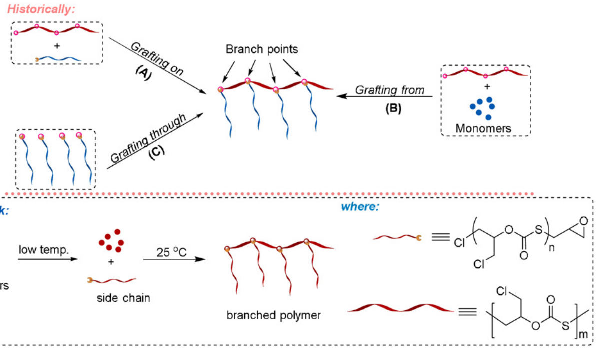
Facile Synthesis of Well-Defined Branched Sulfur-Containing Copolymers: One-Pot Copolymerization of Carbonyl Sulfide and Epoxide

Tian-Jun Yue, Gulzar A. Bhat, Wen-Jian Zhang, Wei-Min Ren, Xiao-Bing Lu, and Donald J. Darensbourg**

Abstract: *Topological polymers possess many advantages over linear polymers. However, when it comes to the poly(monothiocarbonate)s, no topological polymers have been reported. Described herein is a facile and efficient approach for synthesizing well-defined branched poly(monothiocarbonate)s in a "grafting through" manner by copolymerizing carbonyl sulfide (COS) with epichlorohydrin (ECH), where the side-chain forms in situ. The lengths of the side-chains are tunable based on reaction temperatures. More importantly, enhancement in thermal properties of the branched copolymer was observed, as the T_g value increased by 22°C, compared to the linear analogues. When chiral ECH was utilized, semicrystalline branched poly(monothiocarbonate)s were accessible with a T_m value of 112°C, which is 40°C higher than that of the corresponding linear poly(monothiocarbonate)s. The strategy presented herein for synthesizing branched polymers provides efficient and concise access to topological polymers.*

The unique and versatile topological structures of polymers have been facilitating the wide application of synthetic polymers in the fields of biology, drug delivery, smart materials, etc.[1] To this end, synthesizing polymers with diverse topologies in a simplified and efficient way, and then to study how the architecture affects properties of polymer materials have always been an important area of study in polymer chemistry. As one important category of topology polymer, branched polymers have been applied in the field of organic photovoltaics,[2] organic semiconductors,[4] fiber reinforced composites for lightweight components,[3] and organic fuel cells.[5] These applications arise because of their elegant properties, which includes tunable rheological properties and three-dimensional (3D) topological structures, as well as reduced viscosities.[6] For instance, in the context of poly(L-lactide), an important polyester which has the potential to be applied in wound closure, surgical implants, and scaffold and drug delivery owing to its biodegradability, biocompatibility, and good mechanical properties.[7] However, the low degradation rate limits its application in drug-release systems. Thus, its structure has to be modified by synthesizing branched poly(L-lactide) to increase its rheological properties. Traditionally, the methodologies for synthesizing branched polymers involve grafting to, grafting from, and grafting through technologies.[8] Specifically, grafting to refers to coupling the pre-formed side-chains onto the main chain (Scheme 1 A), and the graft polymer prepared by producing side-chains in situ by initiation from pendent groups of the main chain is described as grafting from (Scheme 1 B). And grafting through is the (co)polymerization of appropriate macromonomers (Scheme 1 C). Nevertheless, all the mentioned strategies for the synthesis of branched polymers are tedious because they involve the additional steps of pre-polymerization to obtain either the side-chains or the main chains. Thus, the development of an efficient approach to the synthesis of branched polymers is an important and challenging theme.

The precise synthesis of sulfur-containing polymers has made great progress in view of their outstanding characteristics such as good optical properties, remarkable chemical resistance, and excellent heavy metal capture abilities.[9–15] Poly(monothiocarbonate) is a promising class of sulfur-containing polymers because of its potential biodegradability as it contains ester linkages in the backbones. The main synthetic approaches to poly(monothiocarbonate) include the polycondensation of dithiols and phosgene (or thiophosgene)[16] or the ring-opening polymerization of cyclic thiocarbonates.[17] However, these methods are problematic for the



Scheme 1. Strategies for the synthesis of branched polymers.

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[*] T.-J. Yue, W.-J. Zhang, Prof. Dr. W.-M. Ren, Prof. Dr. X.-B. Lu
State Key Laboratory of Fine Chemicals
Dalian University of Technology
2 Linggong Road
Dalian, 116024 (China)
E-mail: wmren@dlut.edu.cn

T.-J. Yue, Dr. G. A. Bhat, Prof. Dr. D. J. Darensbourg
Department of Chemistry, Texas A&M University
College Station, TX 77843 (USA)
E-mail: djdarens@chem.tamu.edu

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reason that the former one involves toxic reactants and the monomers of the latter process are of low reactivity and nondiverse. The more promising approach was developed by the group of Zhang, involving copolymerization of carbonyl sulfide (COS) with various epoxides, affording the corresponding poly(monothiocarbonate)s with diverse structures.[18] Since then, a series of elegant catalyst systems, such as various metal complexes[18,19] and organic Lewis acid/base pairs,[20] were developed to realize the reaction in a coordination insertion manner, without unpleasant side reactions, which includes O/S exchange reactions and the formation of cyclic products. Furthermore, with the employment of a chiral catalyst, regio- and stereoselectivity can be achieved, providing a series of isotactic poly(monothiocarbonate)s in a crystalline nature with melting temperatures ranging from 96 to 232 °C.[19c,21] Though impressive progress has been made, the poly(monothiocarbonate)s, obtained currently are all linear. The lack of other topological poly(monothiocarbonate)s, like branched poly(monothiocarbonate)s, restricts further applications of such biodegradable polymers. Herein, we describe an efficient strategy for the synthesis of comblike poly(monothiocarbonate)s, for the first time, through the one-pot, two-step copolymerization of COS and epichlorohydrin with tunable side-chain lengths by modulating the temperature at different time points during the reaction (Scheme 1).

To synthesize branched poly(monothiocarbonate)s in a simple and efficient way, the two factors that matter most are the method and the monomer. In fact, among all the methods described for branched polymer formation, graft through shows the best potential for accessing branched polymers in an efficient and predigest way, in which the main chain and side-chain can be synthesized at the same time. Thus, herein we have investigated the graft through method for synthesizing branched poly(monothiocarbonate)s. The following involves screening a suitable monomer, which can convert to both the main chain and side-chain when copolymerizing with COS. In this manner, we have obtained the first crystalline poly(monothiocarbonate) from the copolymerization of optical epichlorohydrin (ECH) and COS with a single-site bifunctional Cr complex as the catalyst.[21a] As described, the obtained poly(monothiocarbonate) is end-capped with an epoxy ring, which was generated by a substitution reaction involving the thiocarbonate ion (-OC(O)S$^-$) at the end of the polymer chain attacking at the chloromethylene of epichlorohydrin, as confirmed by NMR spectroscopy (Figure 1 A). As a consequence, the polymer chain species blocked with an epoxy ring interrupts the chain-propagating process, resulting in a low-molecular-weight poly(monothiocarbonate). Alternatively, the obtained polymer with low molecular weight can be seen as an epoxide with a long flexible chain as the substituent group. In this context, we supposed that the terpolymerization of COS, ECH, and the formed epoxy ring tethered to a polymer chain (assigned as ER) would proceed smoothly and provide the branched poly(monothiocarbonate)s, for which the side-chains are long flexible substituted groups of ER. However, the formed epoxy ring was still observed in the ^{1}H NMR spectrum when the copolymerization of COS and ECH, with the Cr complex as the catalyst, was conducted for 24 hours (Figure 1 A), wherein the ECH conversion was 99 %. This finding is ascribed to the high viscosity of the reaction mixture inhibiting the copolymerization of the high-molecular-weight epoxide (ER) with COS. In view of this, we performed the COS/ECH copolymerization in the presence of toluene as a solvent. As expected, the ER was completely consumed (Figure 1 B), together with the disappearance of the peaks of the carbon signal of the ER in the ^{13}C NMR spectrum (see Figure S1 in the Supporting Information). This observation suggested the formation of branched poly(monothiocarbonate)s, with a molecular weight (M_n) of 15 100 g mol^{-1} and narrowly distributed PDI of 1.31 (Figure 2, left) as determined by gel permeation chromatography (GPC) in THF, calibrated with linear polystyrene standards. The M_n value of the final poly(monothiocarbonate) is much higher than that of the previous one, for which the M_n is 1480 g mol^{-1}. Again, the GPC with four detectors was employed to determine an accurate molecular weight of the resultant poly(monothiocarbonate) and confirm the structure. As showed, the accurate M_n was determined as 36 000 g mol^{-1}. Additionally, the α and K value of linear poly(monothiocarbonate) were determined as 0.339 and 1.02, respectively, with this GPC. Thus, based on the Mark-Houwink equation, the relationship between intrinsic viscos-

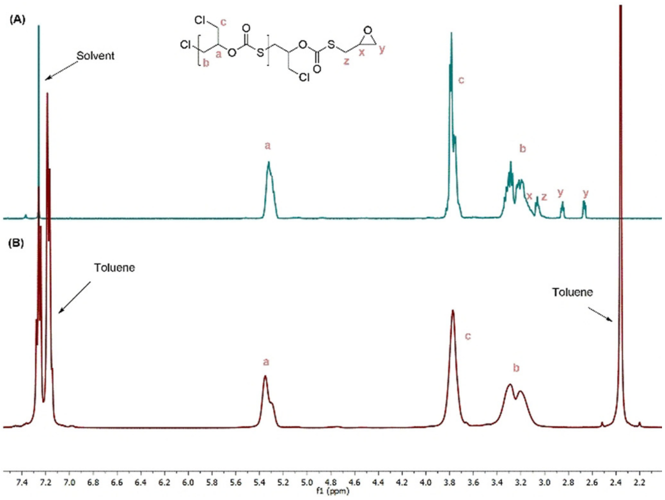


Figure 1. ^{1}H NMR spectra of unpurified copolymers without solvent (A) and with toluene as the solvent (B).

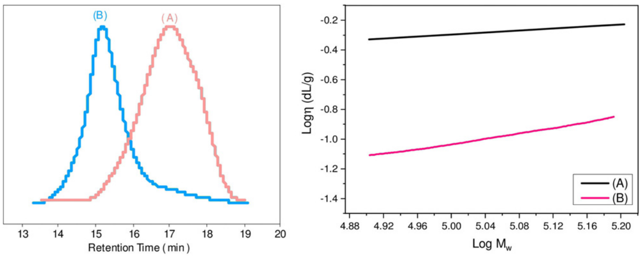


Figure 2. Left: GPC traces for linear poly(monothiocarbonate)s (A) and branched poly(monothiocarbonate)s (B). Right: Relationships of intrinsic viscosities and molecular weights of linear poly(monothiocarbonate)s (A) and branched poly(monothiocarbonate)s (B).

ity and molecular weight of linear and branched poly(monothiocarbonate)s is described (Figure 2, right). As shown, the intrinsic viscosity of the branched poly(monothiocarbonate) is always lower than the corresponding linear poly(monothiocarbonate), suggesting the formation of poly(monothiocarbonate) with a branched structure.

To better understand the copolymerization of COS with ECH, a series of parallel experiments were performed and quenched at the reaction time of 1, 2, 4, 8, 12, 16, and 20 hours. The reaction mixtures were taken out for ^{1}H NMR analysis to monitor the reaction (Figure 3). As can be seen, the epoxy ring is initially visible with peaks at $\delta = 3.10$, 2.74, and 2.65 ppm. The gradually increase in the intensities of peaks representing ER can be clearly observed for up to 8 hours compared to toluene, along with the ECH conversion of 90 %. After that, the intensities of these peaks begin to decline, and last for 20 hours, accompanied by the disappearance of the peaks representing epoxy rings. A detailed study on formation of the branched poly(monothiocarbonate) was carried out using intermittent sampling experiments. The ^{1}H NMR analysis was used to track the polymerization process and explore the reactive relationship between ECH and ER. The content[22] of ECH and ER in the reaction mixture, as well as the M_n values of the resultant copolymers, over time are shown in Figure 4. At the reaction temperature of 25 °C, the copolymerization proceeded quickly, followed by the substitution reaction of the formed propagating monothiocarboxylate species attacking the chloromethylene of epichlorohydrin. This process afforded the polymer chain end capped with the epoxy ring (ER) along with the release of chloride ion at the initial stage of the copolymerization. Within these 9 hours, the consumption of ECH is mainly responsible for the increase in ER (Figure 4 A), suggesting the formation of the side chains during in this period. The M_n values of the resultant side-chains were around 810 g mol^{-1}, with a broad polymer distribution index (Figure 4 B). After that, the continuous reduction of ECH and ER indicated the terpolymerization of ER, ECH, and COS, affording the branched poly(monothiocarbonate). This data agrees with the GPC results, as a dramatic increase in the M_n value of the copolymer was observed, accompanied with a decrease in PDI. This behavior can be attributed to the fact that the copolymerization of ECH and COS is a typical immortal polymerization wherein the chain-transfer process is faster than the chain-propagation process. Thus, more side-chains were incorporated into the main chain during the terpolymerization process, thereby affording the more uniform branched polymers. A similar situation was observed when the intermittent sampling experiments were conducted at a lower temperature of 0 °C (see Figure S2). Noteworthy, for both cases, the molecular weights of the side-chains remained essentially unchanged before the terpolymerization proceeded. However, the M_n values of side-chains obtained at 0 °C were around 1000 g mol^{-1}, which is higher than that of the side chains at 25 °C. It is known that temperature plays an important role on the substitution reactions and often affects the reaction by favoring the substitution process at higher temperature, while, suppressing it at lower temperature. When the copolymerization worked at 0 °C, the substitution process is more suppressed. Thus, the propagating process is favored, affording the side-chains with higher molecular weights.

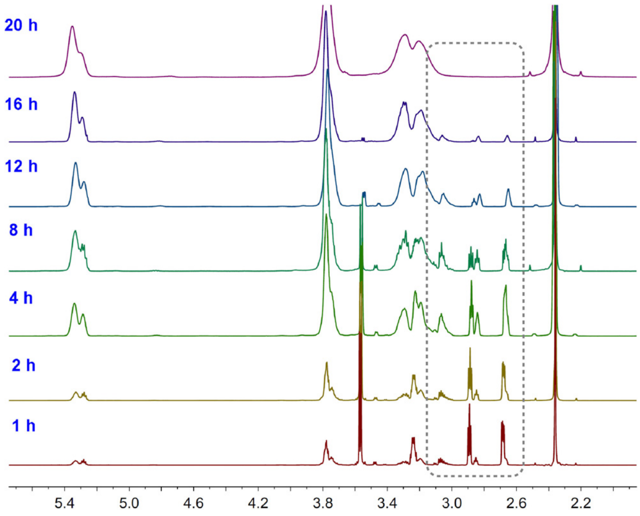


Figure 3. Time-elapsed ^{1}H NMR spectrum of the COS/epichlorohydrin copolymerization in the presence of toluene as solvent at 25 °C.

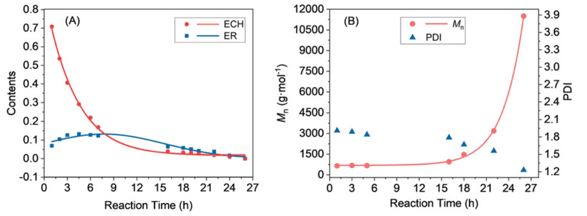
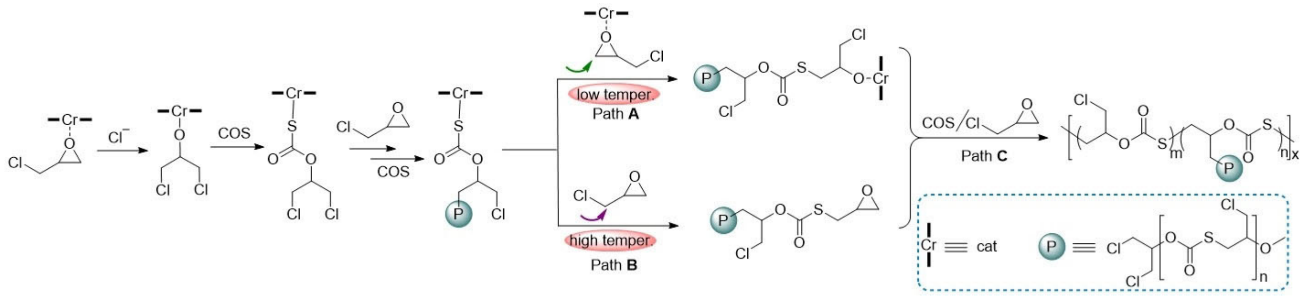


Figure 4. Results of tracking the polymerization process by the intermittent sampling experiments. A) Plots of the ECH and ER contents versus the reaction time at 25 °C. B) The GPC trace of the resultant copolymers.

Based on the description above, the elaborate formation process of branched poly(monothiocarbonate) can be described as follows: the copolymerization starts with the ring opening of ECH, followed by the chain propagation in the initial stage (Scheme 2, Path **A**). The competitive reaction, wherein the thiocarbonate ion attacks the chloromethylene of ECH with the release of chloride, intervened, resulting in an epoxy ring end capped poly(monothiocarbonate), that is, a side-chain. This epoxy capped short chain serves as the side-chain in the latter copolymerization procedure (Path **B**). Finally, the terpolymerization of ECH, ER, and COS proceeded and produced the branched poly(monothiocarbonate)s (Path **C**).

For this copolymerization, reaction temperature greatly influenced the two competitive processes. At a low temperature of 0 °C, the ring opening and substitution reactions are both unfavored, with the latter process suppressed to a great extent. In this case, the chain-propagation process proceeded for a longer time and afforded the side-chains with a higher molecular weight, that is, long side-chains. Whereas at a higher temperature, the substitution reaction is more favored, resulting in the poly(monothiocarbonate)s with a low molecular weight, that is, short side-chains. Owing to



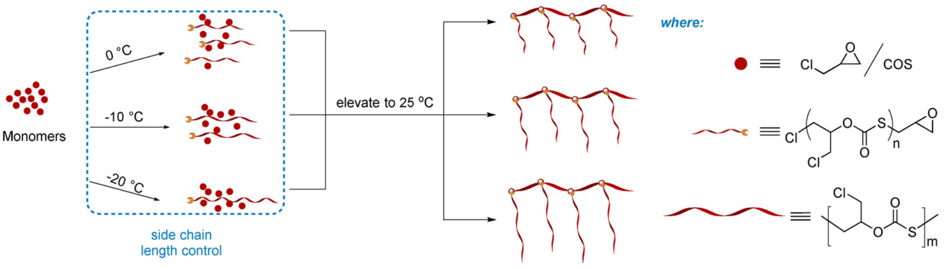
Scheme 2. The pathway for synthesizing branched poly(monothiocarbonate)s.

this fact, the branched poly(monothiocarbonate)s with longer side-chains were attempted to be synthesized by performing the copolymerization at −25 °C. However, the peaks corresponding to ER are still visible in the ^{1}H NMR spectrum (see Figure S3A), meaning the terpolymerization cannot proceed smoothly at −25 °C, probably because the reactivity of ER toward ring opening is too low at low temperature. Fortunately, the ER can be opened at elevated temperature (see Figure S3B). In this regard, the length of the branched poly(monothiocarbonate) can be tuned by performing the copolymerization at different temperatures to obtain side-chains with different lengths before elevating it to 25 °C.

Indeed, the branched poly(monothiocarbonate)s with different side-chain lengths were synthesized according to Scheme 3. Initially, the copolymerizations of ECH and COS were performed at different temperatures ranging from −20 to 0 °C with the feed ratio of ECH/Cat. = 3000:1 for certain times to obtain the branched poly(monothiocarbonate)s with different side-chain lengths. As characterized, at the approximated ECH conversion of 86 %, the molecular weights of the copolymers obtained at reaction temperature of −20, −10, and 0 °C were 1780, 1610, and 1480 g mol^{-1}, respectively (see Figure S4) and the final branched poly(monothiocarbonate)s molecular weights were 12 500, 15 200, and 17 100 g mol^{-1} as determined by gel permeation chromatography in THF, calibrated with linear polystyrene standards (see Figure S5). The accurate molecular weights of these three samples were further confirmed by a GPC with four detectors. Thereby, the accurate molecular weights were 32 900, 36 400, and 37 800 g mol^{-1} (see Figure S6), which are much higher than the M_n values determined by the GPC with ultraviolet (UV) detector, indicating branched polymers were obtained.

Furthermore, the thermal properties of the linear and branched COS/ECH copolymer were compared by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA indicated that the linear COS/ECH copolymer (M_n = 1470 g mol^{-1}) had a 5 % weight loss (T_d) of 247.0 °C (see Figure S7), while for the branched COS/ECH copolymer an enhanced T_d was observed at 261.6 °C. The DSC thermograms showed that the linear COS/ECH copolymer had a T_g of −10.2 °C (see Figure S8), while the T_g of the branched poly(monothiocarbonate)s was increased to 11.3 °C. Additionally, the highlight of the copolymerization of ECH and COS mediated by the Cr-based bifunctional catalyst is the access to isotactic poly(monothiocarbonate)s by using optically active ECH for the copolymerization. Hence, the branched poly(monothiocarbonate) with isotactic side-chains and main chains is also achievable when chiral ECH is used in the copolymerization. Indeed, the isotactic branched poly(monothiocarbonate) was obtained with a melting temperature (T_m) of up to 112.4 °C and a melting enthalpy (ΔH_m) of 47.3 J g^{-1} (Figure 5 B), which are both higher than that of the linear one with a T_m of 82.2 °C with a ΔH_m of 15.1 J g^{-1} (Figure 5 A). This data can be attributed to the fact that the molecular weight of the poly(monothiocarbonate) has an influence on the crystalline behavior of the isotactic poly(monothiocarbonate).[21a] The increase in the molecular weight of the branched poly(monothiocarbonate) facilitated the crystalline behavior of the poly(monothiocarbonate).

In conclusion, we have demonstrated a facile and efficient strategy for synthesizing branched poly(monothiocarbonate)s by a one-pot two-step process, affording the branched poly(monothiocarbonate)s. Interestingly, the lengths of side-chains are tunable by performing the reaction at different temperatures before elevating reaction temperature to 25 °C. Additionally, the branched poly(monothiocarbonate)s show enhanced thermal properties compared to the linear poly(monothiocarbonate)s. The new method presented herein for accessing branched poly(monothiocarbonate)s expands the methodology library for synthesizing branched polymers.



Scheme 3. Synthesizing branched poly(monothiocarbonate) with tunable side-chain lengths and densities.

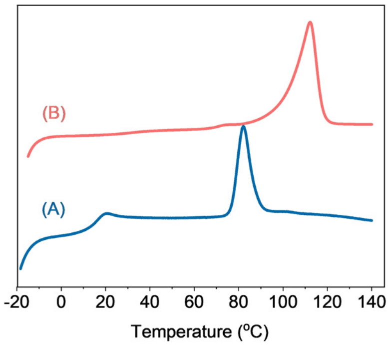


Figure 5. DSC thermograms of COS/(*S*)-ECH copolymers: A) linear copolymer ($M_n = 1470\ \mathrm{g\,mol^{-1}}$) with a T_m of 82.2 °C; B) branched copolymer, ($M_n = 11500\ \mathrm{g\,mol^{-1}}$) with a T_m of 112.4 °C.

Experimental Section

Representative procedures for synthesizing branched poly(monothiocarbonate): A 50 mL Parr autoclave was heated to 120 °C under vacuum for 8 h, cooled under vacuum to room temperature, and moved into the dry box. Catalyst (11.5 mg, 0.015 mmol), epichlorohydrin (7.0 g, 76.5 mmol, 5000 equiv), and toluene (10.0 mL) were placed in an autoclave equipped with a magnetic stirrer. The autoclave was placed in a bath at −25 °C and pressurized with COS (6.9 g, 115.0 mmol). After the allotted reaction time, a small amount of the resultant polymerization mixture was removed from the autoclave for ^{1}H NMR analysis to quantitatively provide the conversion of epichlorohydrin, and it was also used for GPC analysis to determine the length of the side-chains. Subsequently, the reaction was continued at 25 °C for a required time. Again, a small amount of the resultant polymerization mixture was removed from the autoclave for ^{1}H NMR analysis to quantitatively give the conversion of epichlorohydrin and was also used for GPC analysis to determine the molecular weight of the final copolymer. The unpurified polymer was dissolved in a 20 mL of $CHCl_2$/ MeOH (1/1, v/v) mixture with 0.5 % HCl solution and precipitated from methanol. This process was repeated 3–5 times to completely remove the catalyst, and a resulting white polymer was obtained following vacuum drying.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: copolymerization · polymers · epoxides · structure elucidation · synthetic methods

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[22] The contents of ECH and ER in the mixture can be calculated as follows: $c_{(\mathrm{ECH})} = n_{(\mathrm{ECH})}/[n_{(\mathrm{ECH})} + n_{(\mathrm{ER})} + n_{(\mathrm{Poly})} + n_{(\mathrm{cycl.})}]$, $c_{(\mathrm{ER})} = n_{(\mathrm{ER})}/[n_{(\mathrm{ECH})} + n_{(\mathrm{ER})} + n_{(\mathrm{Poly})} + n_{(\mathrm{cycl.})}]$, where: $n_{(\mathrm{ECH})}$, $n_{(\mathrm{ER})}$, $n_{(\mathrm{Poly})}$, $n_{(\mathrm{cycl.})}$ are the molar of residual ECH, ER, poly(monothiocarbonate), and cyclic product, respectively based on the ^{1}H NMR analysis.

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