Nickel-catalyzed polymerization of a substituted sulfoxonium ylide

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Abstract
The homopolymerization of (dimethylamino)phenylsulfoxonium ethylide, a substituted sulfoxonium ylide, is reported. Treatment of the monomer with a readily available Ni(II) catalyst afforded poly[(1-butene)-ran-(2-butene)-ran-(ethylene)] in good yield and high molecular weight. Varying the initial monomer-to-catalyst feed ratio enabled control over the molecular weights of the polymers produced. The polymerization mechanism appears to proceed in a chain growth fashion that entails the addition of ethylide units to growing polymer chains in conjunction with the expulsion of (dimethylamino)phenyl sulfoxide as a byproduct.

KEYWORDS
C1 polymerization, nickel catalyst, poly(methyl methylene), polyhomologation, Sulfoxonium ylides

1 | INTRODUCTION

Synthetic polymers, such as poly(ethylene), poly(styrene), and poly(isobutylene), have found utility in a multitude of omnipresent and specialized applications.1 Such types of polymers are commonly prepared from their constituent olefinic monomers using a polymerization method that effectively grows polymer chains in two carbon increments.2 Although the monomers utilized in such ”C2 polymerizations” are often inexpensive and readily available, they are typically mono- or 1,1-disubstituted alkenes. The use of acyclic 1,2-disubstituted alkenes to afford the corresponding persubstituted polymers remains a challenging endeavor with the exception of dialkyl fumarates, which can be polymerized under certain conditions.3 The difficulty that arises when attempting to polymerize 1,2-disubstituted alkenes can be attributed to steric hindrance. The pendant substituents interfere with the growing (active) chain ends in a manner that obstructs or prevents propagation.3a For example, poly(methyl methylene) can be envisioned as a potential product obtained from the polymerization of 2-butene. However, attempts at polymerizing 2-butene typically afford polymers that feature methyl substituents on every third carbon atom along their main chains.4

Despite the synthetic challenge, poly(methyl methylene) and other persubstituted polymers continue to attract attention. The relatively high density of pendant substituents can be envisioned to facilitate crystallization, reduce conformational flexibility, or alter other intrinsic features that manifest in a range of exotic or novel properties.2,5 It has been hypothesized that persubstituted polymers could be accessed via a C1 polymerization,
which differs from their C2 analogues in that polymer chains are grown in single carbon increments.\textsuperscript{2,5a,5b} Diazocompounds\textsuperscript{6} are commonly used as monomers in C1 polymerizations because nitrogen is released as a byproduct and drives the reaction.\textsuperscript{2,5a} For example, treatment of diazomethane with a catalyst (e.g., copper or BF$_3$) has been reported to afford poly(methylene) (nominally equivalent to poly(ethylene)) and nitrogen as the main products.\textsuperscript{6c,6d} Similarly, approaches to poly(methyl methylene) have also been disclosed (Scheme 1).\textsuperscript{6c,7} For example, diazoethane has been transformed into poly(methyl methylene) although the yield (30–88\%) and molecular weight (5–14 kDa) of the polymer produced appear to depend on the catalyst employed (Lewis acid\textsuperscript{7c} vs. copper,\textsuperscript{6c} respectively.)

Due to the hazards associated with diazoalkanes, attention has shifted toward the use of comparatively stable diazoacetyl derivatives as monomers in C1 polymerizations in conjunction with transition metal-based catalysts.\textsuperscript{6e,8} For example, Inoue has elegantly demonstrated that treatment of alkyl or aryl diazoketones, diazoacetates and diazoacetamides with a range of Pd\textsuperscript{II} catalysts affords the corresponding persubstituted polymers.\textsuperscript{8a,9} De Bruin showed that certain [(N,O-ligand)RhI(diene)] catalysts facilitate the polymerization of ethyl diazoacetate with exquisite stereoregularity and also offer access to high molecular weight derivatives.\textsuperscript{10} Toste, Dichtel, and Denmark, and Wu, recently and independently demonstrated that control over the molecular weights of the polymers obtained from the C1 polymerization of alkyl diazoacetates may be achieved through the use of ($\pi$-allyl)palladium dimers as catalysts.\textsuperscript{6e,8c,11}

Due to their high stability and ease of handling, sulfoxonium ylides\textsuperscript{12} are attractive alternatives for use as monomers in C1 polymerizations.\textsuperscript{5a} Shea showed that poly(methylene) can be obtained by treating sulfoxonium methylide with a trialkylborane. The polymerization reaction is driven by the release of dimethyl sulfoxide as a byproduct and grows in an iterative, homologous fashion; hence the polymerization reaction has been aptly described as a polyhomologation.\textsuperscript{12b,12d} Although the polymerization is controlled and affords well defined polymers, unsubstituted sulfoxonium methylides are typically required which has limited access to persubstituted derivatives.\textsuperscript{12e} Similar restrictions were reported by de Bruin who employed a rhodium based catalyst in lieu of the trialkylborane. Attempts to homopolymerize substituted sulfoxonium ylides, such as ethylides or cyclopropylides, typically result in no reaction.\textsuperscript{12f} Copolymers of methylide and ethylide or cyclopropylide can be prepared;\textsuperscript{12e,12g,12l} however, the polymerization reaction appears to favor the unsubstituted monomer.

\textbf{Previous work}

\textbf{Ray and Matthies}

\begin{align*}
\text{N}_2 & \xrightarrow{\text{Cat.}} \text{Cu or BF}_3\cdot\text{OEt}_2 \\
\text{Shea} & \quad \text{BEt}_3 \\
\text{de Bruin} & \quad \text{CO}_2\text{Et}
\end{align*}

\textbf{This work}

\begin{align*}
\text{1} & \quad \text{THF} \\
\text{2} & \quad \text{Scheme 1 Selected examples of C1 polymerization reactions}
\end{align*}
The recent success of using Group 10 metals to promote C1 polymerizations prompted us to explore the potential of using catalysts containing these metals to facilitate the polymerization of sulfoxonium ethylides. Since Pd and Ni catalysts have been shown to be active in polymerizing diazoesters with bulky substituents, we focused on such types of catalysts to polymerize substituted sulfoxonium ylides. Herein we show that a readily available Ni(II) catalyst, bis(dithiobenzil)nickel(II), may be used to polymerize (dimethylamino)phenylsulfoxonium ethylide (1) and affords a substituted polymer, poly[(1-butene)-ran-(2-butene)-ran-(ethylene)] (2), in good yield and high molecular weight. Moreover, the polymerization reaction appears to proceed in a chain growth fashion that involves the addition of monomer units to growing polymer chains in conjunction with the expulsion of (dimethylamino)phenyl sulfoxide as a byproduct. We will also show that the polymerization reaction can be controlled by varying initial monomer-to-catalyst feed ratio.

2 RESULTS AND DISCUSSION

The synthesis of (dimethylamino)phenylsulfoxonium ethylide (1) is summarized in Scheme 2 and utilizes modifications of previously reported procedures. Treatment of thiophenol (3) with iodoethane under basic conditions afforded ethyl phenyl thioether (4) in a yield of 96%. Subsequent oxidation and condensation with ammonia afforded sulfoximine 5 (87% yield), which was then methylated with Meerwein's salt to afford iminium 6 in 72% yield. Ethylide 1 was generated in situ by treating a THF solution of 6 ([6]0 = 0.3 M) with sodium hydride (1.3 equiv.). The 1H NMR spectrum recorded for 1 featured salient signals at 1.62 and 1.57 ppm (THF-d8), which were assigned to the monomer's methine and methyl groups, respectively. Signals attributed to the phenyl (7.48–7.90 ppm) and N-methyl (2.68 ppm) groups were observed as well (see Figure S11).

In a preliminary test, a range of transition metal complexes were explored for their ability to polymerize 1, and a positive result was obtained with bis(dithiobenzil) nickel(II) (7). The catalyst was added to an anhydrous tetrahydrofuran solution of 1 ([1]0 = 0.30 M; [1]0/[7]0 = 500) and stirred under an atmosphere of nitrogen at 50 °C. The progress of the reaction was periodically monitored until the monomer was fully consumed. After 16 h, the reaction mixture was poured into an excess quantity of acidified methanol, and the precipitate that formed was filtered and dried to afford a yellow solid. A yield of 78% was calculated assuming that the polymer consisted of a repeat unit with an empirical formula of C2H4. The number average molecular weight (Mn,exp) of the material was determined by size exclusion chromatography (SEC) to be significantly higher than its theoretical value (Mn,theory), which assumed quantitative initiation and monomer conversion (c.f., 98.7 vs. 14.0 kDa). The polydispersity index (Đ) value was measured to be 1.82.

The structure of 2 was elucidated using NMR spectroscopy. The 1H NMR spectrum recorded for the material featured signals at 1.29 and 0.87 ppm (CDCl3), which are diagnostic for a combination of methine and methylene as well as methyl groups, respectively (Figure 1(A)). The corresponding 13C NMR spectrum was in accord with those reported for other polyolefins (Figure 1(B)), particularly the polymer obtained via a nickel-catalyzed polymerization of either trans-2-butene or...
The signal observed at 20 ppm (CDCl₃) was consistent with that expected from a methyl group and the series of signals over the range of 33–35 ppm were assigned to methine and methylene groups. The weaker signals observed were attributed to isomers. The polymer appeared to be uniform and linear as a Mark-Houwink plot revealed a strong correlation between the intrinsic viscosity and molecular weight ($R^2 = 0.99$) (see Figure 1(C),(D)). The glass transition temperature of the polymer was determined to be $-50 \degree C$ by differential scanning calorimetry and thermogravimetric analysis revealed that the polymer began to decompose at $412 \degree C$ under nitrogen.

Next, efforts were directed toward optimizing the polymerization conditions; key results are summarized in Table 1. Increasing the reaction temperature to $70 \degree C$.

![Representative (A) $^1$H NMR and (B) $^{13}$C NMR spectra recorded for 2 in CDCl₃ (23 °C). (C) Plot of refractive index (black) and log molecular weight (red) versus retention volume. (D) Mark-Houwink plot. The SEC data were obtained using a polymer with a $M_n$ of 73.6 kDa and a $D$ of 1.71 [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 1** Summary of conditions that were used to polymerize 1

| Entry | $[\text{I}]_0$ (M) | Reaction time | Reaction temperature (°C) | $M_n$ theory (kDa)$^b$ | $M_n$ exp. (kDa)$^c$ | $D$$^c$ | Isolated yield (%)$^d$ |
|-------|-------------------|---------------|---------------------------|------------------------|---------------------|-------|------------------------|
| 1     | 0.30              | 16 h          | 50                        | 14.0                   | 98.7                | 1.82  | 78                     |
| 2     | 0.30              | 4 h           | 70                        | 14.0                   | 62.0                | 2.03  | 85                     |
| 3     | 0.30              | 3 d           | RT                        | 14.0                   | 87.5                | 1.96  | 56                     |
| 4     | 0.10              | 16 h          | 50                        | 14.0                   | 78.0                | 1.86  | 49                     |
| 5     | 0.60              | 2 h           | 50                        | 14.0                   | 54.5                | 2.08  | 66                     |
| 6     | 0.60              | 5 d           | RT                        | 14.0                   | 56.6                | 2.04  | 83                     |

$^a$General reaction conditions: $[\text{I}]_0/[\text{I}]_0 = 500$; solvent: THF; nitrogen atmosphere.

$^b$The theoretical $M_n$ values were calculated based on the $[\text{I}]_0/[\text{I}]_0$ feed ratio. Conversions were > 99% as determined by testing for residual monomer using phenolphthalein.

$^c$The values were obtained using SEC in THF and are reported against poly(styrene) standards.

$^d$Isolated yield.

1-butene (vide infra). The signal observed at 20 ppm (CDCl₃) was consistent with that expected from a methyl group and the series of signals over the range of 33–35 ppm were assigned to methine and methylene groups. The weaker signals observed were attributed to isomers. The polymer appeared to be uniform and linear as a Mark-Houwink plot revealed a strong correlation between the intrinsic viscosity and molecular weight ($R^2 = 0.99$) (see Figure 1(C),(D)). The glass transition temperature of the polymer was determined to be $-50 \degree C$ by differential scanning calorimetry and thermogravimetric analysis revealed that the polymer began to decompose at $412 \degree C$ under nitrogen.
resulted in slightly higher yields (85%) and shorter reaction times (4 h) but produced a relatively low molecular weight polymer with a broader polydispersity ($M_n = 62.0$ kDa; $D = 2.03$). In contrast, decreasing the reaction temperature to ambient afforded a polymer with an $M_n$ value similar to that obtained at 50 °C, albeit in lower yield (56%), and a longer reaction time (3 days) was required. With negligible improvements being observed through temperature variation, subsequent efforts were directed toward varying the initial monomer concentration. The use of relatively high initial monomer concentrations resulted in decreased polymer yield (66%). Likewise, lowering the initial concentration also led to a yield reduction (49%). While varying both the concentration and temperature afforded a relatively high yield of polymer (83%), long periods of time (5 days) were necessary. Thus, we concluded that the initial parameters selected provided optimal results and, as such, subsequent experiments utilized these conditions.

The kinetics of the polymerization reaction were measured by monitoring the consumption of monomer over time and under various conditions using $^1$H NMR spectroscopy. Based on the data shown in Figure 2(A), the initial stage of reaction was found to be zero order with respect to monomer (1) and first order with respect to catalyst (7), and appeared to reach a steady-state after approximately 1 h (see Figure S3). The molecular weights of the polymers produced over time were also assessed by periodically removing aliquots from a reaction mixture (conducted in THF-d$_8$) followed by

**FIGURE 2**  (A) Plot of $\ln$ [monomer] versus time. Conditions: pink and red lines, $[1]_0 = 0.10$ M; 50 °C; blue line, $[1]_0 = 0.20$ M; 50 °C. (B) Plot of $M_n$ versus monomer conversion. Conditions: $[1]_0 = 0.30$ M; 50 °C; $[1]_0/[7]_0 = 500$. (C) Plot of $M_n$ versus the initial monomer-to-catalyst ratio. Conditions: $[1]_0 = 0.30$ M; 50 °C. The experimental $M_n$ and $D$ values were obtained using SEC. The theoretical $M_n$ values assumed quantitative initiation and that the empirical formula of the polymer repeating unit was C$_2$H$_4$. (D) Size exclusion chromatograms recorded for a series of polymers that were prepared by varying the monomer-to-catalyst feed ratio (indicated). Conditions: $[1]_0 = 0.30$ M; 50 °C; 16 h. Isolated yields were typically >49% [Color figure can be viewed at wileyonlinelibrary.com]
analyzing those aliquots using $^1$H NMR spectroscopy as well as SEC. As shown in Figure 2(B), the molecular weights of polymers were relatively high and approximately constant over the course of the reaction. To determine if the polymer molecular weight can be controlled, the monomer-catalyst feed ratios were systematically varied from 25 to 750. Although higher than their theoretical values, the $M_n$ values increased with the feed ratio while the corresponding $D$ values remained relatively constant (1.7 to 2.3). Collectively, these data indicated that the polymerization proceeded in a chain-growth fashion but may suffer from a relatively low initiation efficiency.

To gain a deeper understanding of the underlying polymerization mechanism, the reaction was monitored over time using $^1$H NMR spectroscopy (Figure 3(A)). Upon the addition of 7 to a THF-$d_8$ solution of the monomer, decreases in intensity were observed for the signals assigned to the ylide (1.57, 1.62, 2.68, 7.48–7.90 ppm) while new signals which corresponded to the polymer (0.89, 1.34 ppm) and the expected byproduct, (dimethylamino)phenyl sulfoxide, (2.56, 7.47–7.64 ppm), formed. Close inspection of the spectra recorded after 20 h of reaction time revealed the appearance of two new signals at 5.4119 and 1.57 ppm, which were assigned to 2-butene (Figures 3(B)-(D)). Thus, we hypothesized that 1 initially underwent dimerization to form butene before undergoing polymerization. Since the polymerization was rapid and 2-butene was not observed during early stages, separate efforts were directed toward polymerization of trans and cis-2-butene using 7. Exposure of either alkene to the catalyst did not result in monomer consumption and did not afford a polymeric product. A similar outcome was obtained when 1-butene (which presumably could arise via the isomerization of 2-butene) was treated with 7. It was also reasoned that the reaction between 1 and 7 may generate an active catalyst in situ that is capable of polymerizing 2-butene. To test, 1 was first polymerized using aforementioned conditions. When the reaction reached completion, an aliquot was removed and trans-2-butene was added to the residual mixture ($\frac{[\text{trans}-2\text{-butene}]}{[1]} = 6$). After 12 h, the mixture was first analyzed via $^1$H NMR spectroscopy, which revealed that trans-2-butene was still present, and then poured into methanol to facilitate the precipitation of the polymer product. The $M_n$ values measured for the polymer contained in the aliquot and that in the treated mixture were similar (82.8 vs 83.5 kDa, respectively; Figure S4). The addition of 2-butene also did not significantly affect the yield of the polymer product (70%; c.f., Table 1, Entry 1).

Based on the aforementioned results, a potential polymerization mechanism was devised and is shown in Scheme 3. Insertion of monomer 1 into 7 accompanied by the release of (dimethylamino)phenyl sulfoxide results in the formation of 8. The intermediate may then add another monomer unit or undergo isomerization. If the former occurs, then a subsequent metal migration event adds a repeat unit with a branched structure, labeled as A ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), to the growing polymer chain. Alternatively, isomerization of 8 to 9 followed by monomer addition should afford intermediate 10. Subsequent metal migration to either the terminal or the antepenultimate position should effectively extend the growing polymer with either a linear or branched repeat unit, designated as B ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) or C ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), respectively.
3 | CONCLUSIONS

In summary, we have developed a method that enables the polymerization of a substituted sulfoxonium ylide. The corresponding polymer was obtained in good yield and in high molecular weight. The polymerization reaction employed a nickel-based catalyst and proceeded in a chain-growth fashion to afford linear polymers with a multitude of substituents along the backbone. The polymerization reaction can be controlled by varying the initial monomer-to-catalyst feed ratio, although the molecular weights of the polymers produced are typically higher than their theoretical values. Finally, the polymerization mechanism appears to proceed in a chain growth fashion wherein monomer units are added to growing polymer chains while expelling (dimethylamino)phenyl sulfoxide as an expected byproduct. In a broader perspective, the results support the hypothesis that the use of transition metal complexes in lieu of boron-based Lewis acids can promote the C1 polymerization of substituted ylides, although steric congestion in growing polymer chains may facilitate isomerization. Future work will focus on varying the ligand environment21 to manage steresics in a manner that suppresses isomerization and promotes the formation of polymer chains that feature repeat units with relatively high degrees of substitution and stereoregularity.

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CONFLICT OF INTEREST
The authors declare no potential conflict of interest.

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REFERENCES
[1] a) I. Cooper, in Chemical Migration and Food Contact Materials (Eds: K. A. Barnes, C. R. Sinclair, D. H. Watson), Cambridge, UK, Woodhead Publishing, 2007, p. 228. b) N. C. Paxton, M. C. Allenby, P. M. Lewis, M. A. Woodruff, Eur. Polym. J. 2019, 118, 412.
[2] C. R. Cahoon, C. W. Bielawski, Coord. Chem. Rev. 2018, 374, 261.
[3] a) N. Toyoda, M. Yoshida, T. Otsu, Polym. J. 1983, 15, 255. b) A. Matsumoto, Y. Sano, M. Yoshioka, T. Otsu, J. Polym. Sci., Part A: Polym. Chem. 1996, 34, 291. c) T. Otsu, T. Yasuhara, A. Matsumoto, J. Macromol. Sci. Chem. 1998, A25, 537.
[4] a) K. Endo, Y. Kondo, Polym. J. 2006, 38, 1160. b) W. Liu, M. Brookhart, Organometallics 2004, 23, 6099.
[5] a) E. Jellema, A. L. Jongerius, J. N. Reek, B. de Bruin, Chem. Soc. Rev. 2010, 39, 1706. b) E. Ihara, H. Shimomoto, Polymer 2019, 174, 234. c) M. Burns, S. Essafi, J. R. Bame, S. P. Bull, M. P. Webster, S. Baileu, J. W. Dale, C. P. Butts, J. N. Harvey, V. K. Aggarwal, Nature 2014, 513, 183. d) E. Ihara, R. Okada, T. Sogai, T. Asano, M. Kida, K. Inoue, T. Itoh, H. Shimomoto, Y. Ishibashi, T. Asahi, J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 1020.
[6] a) D. G. Hetterscheid, C. Hendriksen, W. I. Dzik, J. M. Smits, E. R. van Eck, A. E. Rowan, V. Busico, M. Vacatello, V. Van Axel Castelli, A. Segre, E. Jellema, T. G. Bloemberg, B. de Bruin, J. Am. Chem. Soc. 2006, 128, 9746. b) E. Ihara, M. Kida, T. Itoh, K. Inoue, J. Polym. Sci., Part A: Polym. Chem. 2007, 45, 5209. c) G. D. Buckley, L. H. Cross, N. H. Ray, J. Am. Chem. Soc. 1950, 72, 2714. d) S. W. Kantor, R. C. Osthoff, J. Am. Chem. Soc. 1953, 75, 931. e) J. H. Chu, X. H. Xu, S. M. Kang, N. Liu, Z. Q. Wu, J. Am. Chem. Soc. 2018, 140, 17773. f) J. Bai, L. D. Burke, K. J. Shea, J. Am. Chem. Soc. 2007, 129, 4981.
[7] a) A. G. Nasini, G. Saini, L. Trossarelli, Pure Appl. Chem. 1962, 4, 255. b) A. G. Nasini, L. Trossarelli, G. Saini, Makromol. Chem. 1961, 44, 550. c) C. E. H. Bawn, A. Ledwith, P. Matthies, J. Polym. Sci. 1956, 40, 1393.
[9] E. Ihara, T. Hiraren, T. Itoh, K. Inoue, *J. Polym. Sci., Part A: Polym. Chem.* 2008, 40, 1094.
[10] E. Jellema, P. H. Budzelaar, J. N. Reek, B. de Bruin, *J. Am. Chem. Soc.* 2007, 129, 11631.

[11] N.-N. Li, X.-L. Li, L. Xu, N. Liu, Z.-Q. Wu, *Macromolecules* 2019, 52, 7260.

[12] a) K. J. Shea, *Chem. – Eur. J.* 2000, 6, 1113. b) K. J. Shea, J. W. Walker, H. Zhu, M. Paz, J. Greaves, *J. Am. Chem. Soc.* 1997, 119, 9049. c) R. B. Zhao, Y. Zhang, J. Chung, K. J. Shea, *ACS Macro Lett.* 2016, 5, 854. d) B. B. Busch, M. M. Paz, K. J. Shea, C. L. Staiger, J. M. Stoddard, J. R. Walker, X. Z. Zhou, H. Zhu, *J. Am. Chem. Soc.* 2002, 124, 3636. e) X. Z. Zhou, K. J. Shea, *J. Am. Chem. Soc.* 2000, 122, 11515. f) A. I. O. Suarez, M. P. del Rio, K. Remerie, J. N. H. Reek, B. de Bruin, *ACS Catal.* 2012, 2, 2046. g) R. Sulc, X.-Z. Zhou, K. J. Shea, *J. Am. Chem. Soc.* 2000, 122, 11515. h) J. Luo, K. J. Shea, *Acc. Chem. Res.* 2010, 43, 1420. i) J. Luo, R. B. Zhao, K. J. Shea, *Macromolecules* 2014, 47, 5484. j) D. Wang, Z. Zhang, N. Hadjichristidis, *Polym. Chem.* 2017, 8, 4062. k) J. J. Tufariello, L. T. C. Lee, *J. Am. Chem. Soc.* 1966, 88, 4757. l) R. B. Zhao, K. J. Shea, *ACS Macro Lett.* 2015, 4, 584. m) X.-Z. Zhou, K. J. Shea, *Macromolecules* 2001, 34, 3111.

[13] F. Kato, A. Chandra, M. Tokita, H. Asano, H. Shimomoto, E. Ihara, T. Hayakawa, *ACS Macro Lett.* 2018, 7, 37.

[14] a) P. R. Blakemore, M. S. Burge, *J. Am. Chem. Soc.* 2007, 129, 3068. b) J. F. Lohier, T. Glachet, H. Marzag, A. C. Gaumont, V. Reboul, *Chem. Commun.* 2017, 53, 2064. c) C. R. Johnson, E. R. Janiga, *J. Am. Chem. Soc.* 1973, 95, 7692.

[15] Precipitation in degassed methanol did not give rise to significant differences in molecular weights or D values.

[16] a) P. Wehrmann, S. Mecking, *Macromolecules* 2006, 39, 5963. b) L. P. Lindeman, J. Q. Adama, *Anal. Chem.* 2002, 43, 1245.

[17] M. E. Cangussu, A. P. de Azeredo, A. G. Simanke, B. Monrabal, *Macromol. Symp.* 2018, 377, 1700021.

[18] Adding (dimethylamino)phenyl sulfoxide to the polymerization reaction did not appear to be detrimental to catalyst performance. Conditions: [1]0 = ([dimethylamino]phenyl sulfoxide)0 = 0.3 M; [7]0/[7]0 = 500; 50 °C; 16 h. Yield of 2 (with addition of (dimethylamino)phenyl sulfoxide) = 75%; Mn = 53.4 kDa; D = 1.76. Yield of 2 (without addition of (dimethylamino)phenyl sulfoxide) = 79%. Mn = 65.4 kDa. D = 1.72.

[19] Using diffusion-ordered spectroscopy (DOSY), the diffusion coefficient of the polymer was measured to be smaller than that of the unsaturated (alkenyl) byproduct(s) (c.f., 1.78 × 10−10 vs 1.22 × 10−9 m² s⁻¹, respectively) (see Figure S13).

[20] K. Wang, E. I. Stiefel, A. O. Patil, S. Zushma (ExxonMobil Research and Engineering Company), U.S. Patent 6,743,960 B2, 2004.

[21] a) Z. Guan, P. M. Cotts, E. F. McCord, S. J. McLain, *Science* 1999, 283, 2059. b) L. Guo, S. Dai, X. Sui, C. Chen, *ACS Catal.* 2016, 6, 428.

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