Homochiral Helical Poly(thiophene)s Accessed via Living Catalyst-Transfer Polymerization

Matthew D. Hannigan, Jada A. Sampson, Lasya Damaraju, and Marcus Weck

[a] Dr. M. D. Hannigan, J. Sampson, L. Damaraju, Prof. Dr. M. Weck
Molecular Design Institute, Department of Chemistry
New York University
New York, NY 10003, United States
E-mail: mw125@nyu.edu

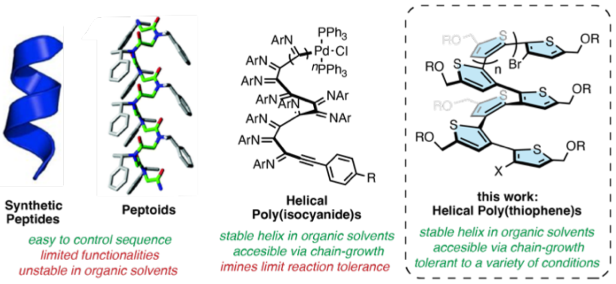
Supporting information for this article is given via a link at the end of the document.

Abstract: Synthetic helical polymers form compact, ordered, and inherently chiral structures, enabling their uses in biomimetic applications as well as catalysis. A challenge in using synthetic helical polymers, however, is their tendency to be sensitive to pH and the presence of nucleophiles, Lewis-acids, or metal ions. We report a strategy to overcome these shortcomings by adapting catalyst-transfer polymerization, a living chain-growth polymerization typically used to access linear conjugated polymers, for the synthesis of helical poly(thiophene)s. We demonstrate that the helical poly(thiophene)s can be synthesized with a single helicity, incorporated into block copolymers, and functionalized at the chain-ends, enabling further conjugation and functionalization. The helical poly(thiophene)s are stable to a variety of conditions, providing benefits over other helical polymers which contain sensitive imine or carbonyl-based functional groups. We anticipate that the ability to access homochiral, heterotelechelic helical conjugated polymers and copolymers will enable new uses of these materials in optoelectronics as well as in applications for mimicking biomacromolecules and other polymers with precisely defined sequences.

The structure and function of many biomacromolecules including proteins and nucleic acids are dictated by a hierarchy made up of primary structure (i.e., the sequence of amino acids or nucleotides), secondary structure (i.e., coils, sheets, helixes, turns, etc.), and tertiary structure (i.e., the folded 3-dimensional shape of the entire macromolecule).[1, 2] From this structural hierarchy, the complex functions of biomacromolecules arise including selective catalysis, chemosensing, molecular transport, and other processes necessary for life.[3] In abiotic systems, however, (e.g., a reaction flask) natural biomacromolecules have limitations including the loss of function in nonaqueous environments and a limited monomer pool,[4] limiting some uses of natural biomacromolecules in applications like chemical synthesis or analysis.

Accessing structural hierarchy in non-natural polymeric systems allows for the development of macromolecules that mimic or complement the complex structures and functions of biomacromolecules while offering increased stability, tolerance to non-aqueous solvents, and functional group diversity.[5] Approaches to realize this structural hierarchy in synthetic systems have mostly focused on amide-based polymers, particularly peptides and peptoids which mimic the monomer structure of natural proteins and enzymes.[6] Other synthetic approaches, including single-chain nanoparticles (SCNPs)[5, 7] and foldamers, have largely fallen short of enabling access to functional tertiary structures.[4, 8] Our group has developed an alternative method to mimic tertiary structure by targeting polymers with inherent secondary structures (i.e., sheets, coils, or helices) via living polymerization methods (which enable control over primary structure).[9] This strategy has enabled access to a variety of polymers containing folded regions of sheets, helices, and coils.[10, 11, 12, 13] A limitation toward accessing functional polymers via our method, however, has been the identity of the helical building blocks.

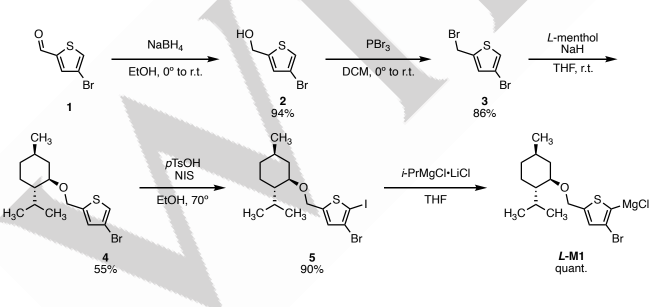
Helical polymers are used in a variety of applications including in chiroptics,[14, 15] catalysis,[16, 17] and chemical separations.[18] Despite the broad uses, most helical polymers that can be synthesized using living polymerizations contain electrophilic functional groups (e.g., carbonyls, imines), which limits functional group tolerance of the resulting polymers.[9, 17] For example, poly(isocyanide)s, a common helical polymer, contain imine functional groups along the backbone and are sensitivity to hydrolysis, oxidation, and attack by nucleophiles. These issues together with their ability to coordinate metals make poly(isocyanide)s challenging to use in a variety of reaction conditions and prevents the use of metal coordination to direct folding. As such, we were motivated to investigate alternative helical polymers that remain helical and stable under a variety of reaction conditions, can be functionalized easily at both chain-ends, and can be accessed via living chain-growth polymerization.



Scheme 1. Commonly reported synthetic helical polymers and their limitations compared to the helical poly(thiophene)s reported in this contribution.

Poly(arene)s, such as poly(thiophene) and poly(phenylene), are polymers that are tolerant to strong nucleophiles, electrophiles, acids, and bases. Additionally, many poly(arene)s can be synthesized via living catalyst-transfer polymerization (CTP)[19] with a wide variety of functional groups and sequence.[20] As such, we envisioned CTP could be a strategy toward reaction-tolerant *helical* polymers via living polymerization. Herein, we describe the synthesis of helical poly(thiophene)s via Ni-catalyzed living CTP, resulting in polymers with narrow dispersities and control over end-groups at both the initiating and terminating ends. Additionally, the polymers synthesized are homochiral (i.e., single-handed) helices and tolerant of a variety of reaction conditions without affecting helicity or molecular weights. We anticipate this strategy towards a new class of functional helical polymers will be useful for accessing biomimetic polymer assemblies as well as for applications in which functionalized helical polymers are required.

We focused on helical poly(thiophene)s because of previous work by Zhang and coworkers in which a non-chiral thiophene was polymerized to yield a helical poly(thiophene) with alternating helical sense.[21] In their work, the reported the use of a Suzuki chain-growth polymerization, deviations from ideal behavior were evident (see SI section IV.ii) and the isolated polymers alternated between left- and right-handed helices along their length. We therefore decided to use a monomer containing a chiral side-chain, and a Kumada-based CTP strategy to access helical poly(thiophene)s with narrow dispersities and molecular weight control. Ultimately, we decided on the *L*-menthol derived monomer ***L*-M1,** which was synthesized as described in Scheme 2. While in the case of an achiral side-chain the left- and right-handed helixes are enantiomeric (and therefore, the helices are equal in energy), we anticipated that the chiral centers and bulk in the side-chain of ***L*-M1** would cause the left- and right-handed helices to be diastereomeric, creating an energetic preference for one helical sense over the other. As such, we anticipated that polymerization of ***L*-M1** would yield *homochiral* helical polymers.



Scheme 2. Synthesis of *L*-menthol derived monomer, ***L*-M1**. The enantiomer, ***D*-M1**, was synthesized via the same procedure but with *D*-menthol.

We screened five catalysts for the polymerization of ***L*-M1**, targeting **P1** polymers with 25-repeat units (denoted as **P1$_{25}$**): two bidentate phosphine catalysts, Ni(dppe)Cl$_2$ and Ni(dppp)Cl$_2$; two N-heterocyclic carbene-based catalysts, Pd-PEPPSI-IPr and Ni(IPr)(PPh$_3$)Cl$_2$; and one monodentate phosphine catalyst, Pd(P(t-Bu$_3$))o-tolBr. These catalysts have been reported to yield linear poly(thiophene)s via living CTP.[22, 23, 24, 25] Surprisingly, despite their reported performance to yield linear poly(thiophene)s, Ni(dppe)Cl$_2$, Ni(dppp)Cl$_2$, and Pd(P(t-Bu$_3$)o-tolBr did not polymerize ***L*-M1** at all as determined by gel-permeation chromatography and showed poor (<10%) monomer conversion (Table 1). Pd-PEPPSI-IPr and Ni(IPr)(PPh$_3$)Cl$_2$ did polymerize ***L*-M1**, although with lower apparent molecular weights than targeted. We hypothesize that the difference in reactivity between the Ni bidentate phosphine complexes and the Ni and Pd NHC complexes can be explained by the relative steric bulk of the ancillary ligands, with bidentate phosphines being more bulky than the NHC ligands, evidenced by their $\%V_{\mathrm{bur}}$ (Table 1).[26] The increased steric bulk of ***L*-M1** (compared to other monomers common in CTP) around the MgCl due to the "large" Br in the ortho position likely prevents the monomer from reacting with the bulkier phosphine-based catalysts. This is supported by work from Kiriy and coworkers investigating the impact of steric bulk on thiophene polymerizations, in which bulkier thiophene monomers were unable to react with Ni catalysts in CTP.[27]

Table 1. Catalyst screening for the CTP of ***L*-M1**, targeting **P1$_{25}$**.

Catalyst	GPC M_n g/mol	GPC $Đ$	% ***L*-M1** conversion	$\%V_b$ of ancillary ligand
Ni(dppe)Cl$_2$	901	1.03	4.4%	50 %
Ni(dppp)Cl$_2$	1,021	1.07	6.2%	54 %
Pd(P(*t*-Bu$_3$))*o*-tolBr	1,102	1.17	8.7%	49%
Pd-PEPPSI-IPr[a]	3,069	1.24	88.9%	42%
Ni(IPr)PPh$_3$Cl$_2$[a]	4,780	1.06	91.5%	45%

[a] IPr ligand = 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene

Next, we performed experiments using the NHC-based catalysts to establish whether polymers of ***L*-M1** can be accessed via living CTP. Pd-PEPPSI-IPr failed to polymerize ***L*-M1** in a living fashion with evidence for catalyst dissociation as the operative termination pathway (Figure S2). Polymerizations with Ni(IPr)(PPh$_3$)Cl$_2$ (Figure 1a), however, showed living polymerization behavior (Figure 1d). Molecular weights varied linearly with the [monomer]/[catalyst] ratio (Figure 1e). Dispersities observed were narrow over the whole range of molecular weights ($Đ$ < 1.08) and molecular weights depended linearly on monomer conversions (Figure 1f). The dispersities from the CTP of ***L*-M1** with Ni(IPr)(PPh$_3$)Cl$_2$ are significantly lower than the dispersities reported for most linear poly(thiophenes) ($Đ$ > 1.17)[28] or previously reported helical poly(thiophene)s ($Đ$ > 1.29).[21] We hypothesize that this is due to the mechanistic differences between helical and linear polymerizations (see SI, section V) as well as the choice of a highly active Ni catalyst which enhances the rate of polymerization.[24]

In addition to these experiments with Ni(IPr)PPh$_3$Cl$_2$, we were able to access linear-block-helical poly(thiophene) copolymers (**P2-b-P1**) by sequential addition of **M2** (a conventional monomer used to access poly(3-hexylthiophene) via CTP) and ***L*-M1** to a solution of Ni(IPr)PPh$_3$Cl$_2$ (Figure 1b). GPC analysis demonstrates that chain-extension enabled access to block copolymers (Figure 1g), providing further evidence of the living behavior of the polymerization of ***L*-M1**. We also attempted to access the same polymer, **P2-b-P1,** using Ni(dppe)Cl$_2$ to probe whether the inability to access **P1** with Ni bidentate phosphines was due to issues with the initiation or propagation with ***L*-M1** (SI Section IV.vii). We were unable to chain-extend **P2–Ni(dppe)Cl** by addition of ***L*-M1**, indicating that the propagation step (not just initiation) with Ni(dppe)Cl$_2$ is hindered by the steric bulk of the bromine adjacent to the nucleophile in ***L*-M1**. Additionally, we attempted to access the reversed-sequence polymers, **P1-b-P2** block copolymers, with Ni(IPr)PPh$_3$Cl$_2$ by initiation with ***L*-M1** followed by addition **M2** (see SI section IV.viii). The resulting polymers, however, showed increased dispersity, indicating loss of chain-growth behavior. Similar behavior, in which switching the block-order has a dramatic effect on dispersity and livingness, has been reported in CTP literature for the copolymerization of benzene and pyrrole[29] or benzene and thiophene[30] via CTP.

Electronic circular dichroism (ECD) spectroscopy of the polymers is significantly different from that of the monomer precursor (**5**) demonstrates that the polymers form helices (Figure 2a) with Cotton effects centered around 340 nm and 300 nm, matching the absorbance bands of the polymer backbone from UV-vis spectra (Figure S20). These results indicate that the backbone of the polymer forms a left-handed helix. When the enantiomer of ***L*-M1**, monomer ***D*-M1**, is used in the CTP with Ni(IPr)(PPh$_3$)Cl$_2$ to give **P3** (Figure 1c), the opposite ECD spectra are observed for **P1**$_{25}$ indicating that a right-handed helix forms. Further, a 1:1 mixture of ***L*-M1** and ***D*-M1** results in the formation of the statistical copolymer, **P4**, with minimal response in the ECD spectrum. The helical structure is even maintained in copolymers, as observed in the ECD spectrum of **P2-b-P1** (Figure 2b). Other polymers **P5**–**P8** were also synthesized from solutions containing varying ee (by mixing of ***L*-M1** and ***D*-M1**) and a ECD of these polymers is provided in the supporting information (SI Section IV.vi). Combined, these results indicate that the identity and chirality of side chains has a dramatic effect on the helical sense of the backbone.

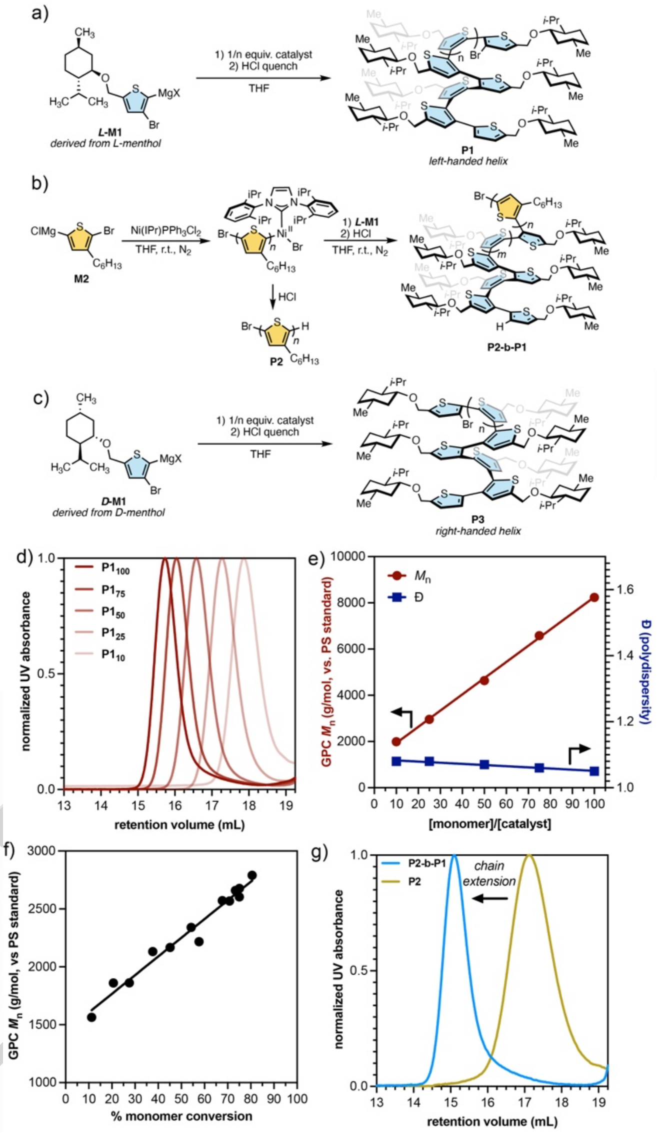


Figure 1. (a) Schematic representation of the synthesis of **P1** (b) **P2**, **P2-b-P1**, and (c) **P3.** (d) GPC chromatograms of **P1**$_{10}$, **P1**$_{25}$, **P1**$_{50}$, **P1**$_{75}$, and **P1**$_{100}$ (e) Plot of molecular weight and dispersity of **P1** vs. catalyst loading, showing a linear relationship; (f) plot of molecular weight vs. % monomer conversion for **P1**$_{25}$ with dashed lines representing the 95% confidence interval for the line of best fit. (g) GPC chromatograms of **P2**$_{20}$ (yellow) and **P2**$_{20}$**-b-P1**$_{100}$ (blue) showing successful chain-extension.

To determine if the polymers were helical throughout their length, (i.e., homochiral) rather than random coils with helical subregions, we performed ECD studies with **P1** at varying molecular weights. We hypothesized that if the polymers were helical along their entire length, then the ECD traces of **P1** at equal concentration (when plotted in units of m°) should be the same, regardless of molecular weight, because the concentration of helical repeating units should be the same in all samples. If the polymers were not helical, however, and instead were random coils with a preference for some limited helical conformations, the ECD traces of **P1** should not overlap, and instead should decrease in intensity with increasing molecular weight (due to the larger conformational entropy of longer polymers leading to a higher concentration of non-helical conformers). When we performed these ECD studies, we found that the ECD traces (plotted in units of m°, Figure 2c) of **P1$_{25}$, P1$_{50}$, P1$_{75}$,** and **P1$_{100}$** overlapped, indicating that the concentration of helical repeating units is constant in all solutions, consistent with polymers that are helical along their length. Further, when plotted in units of molar ellipticity (°cm^{2}dmol^{-1}, Figure 2d), the intensity increases with increasing molecular weight indicating that higher molecular weight polymers have a higher concentration of helical subunits, consistent with *homochiral* helixes. The ECD traces of **P1$_{10}$** deviate from the other polymers, and we ascribe this to the smaller size of the helix in **P1$_{10}$** leading to a less well-defined secondary structure.

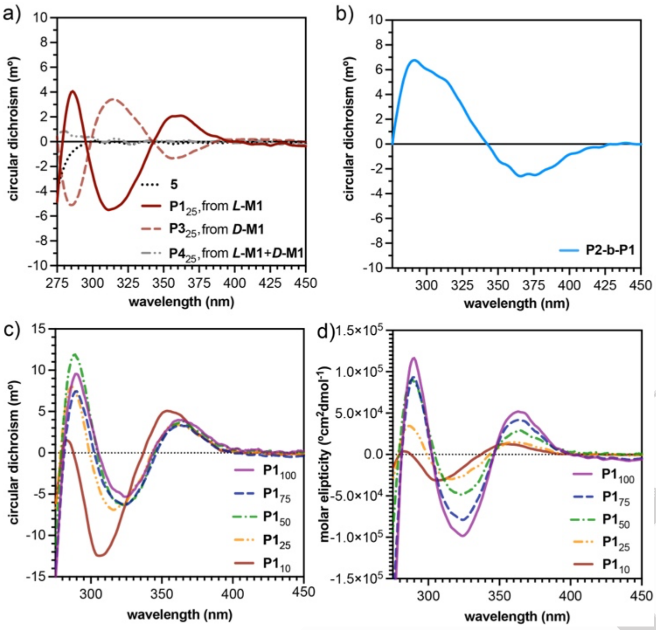


Figure 2. Circular dichroism spectra of (a) **P1$_{25}$, P3$_{25}$, P4$_{25}$**, and **5**; (b) Circular dichroism spectrum of **P2$_{20}$-b-P1$_{100}$**; EDC spectra of **P1$_{10-100}$** in (c) units of m° and (d) molar ellipticity. All ECD spectra were taken in THF at a concentration of 1 mg/mL in quartz cuvettes at r.t.

To demonstrate the increased tolerance of the polymers to a variety of reaction conditions, **P1$_{25}$** was exposed to conditions that other helical polymers, such as poly(isocyanide), poly(acryalamide), and poly(aryl acetylene) polymers, do not tolerate, and CD spectra were measured to probe changes in **P1$_{25}$** helicity. **P1$_{25}$** was exposed to three conditions i) 0.5 M HCl for 12 hours, ii) 0.5 M KO*t*-Bu for 12 hours, and iii) reflux in THF for 12 hours. The CD spectra obtained measured after exposure to these conditions showed only slight differences to the original untreated spectra. The helical sense and molecular weights are maintained in all cases (Figure 3). These results suggest that **P1** is stable against acid, base, heat, and strong nucleophiles (given that these polymers are synthesized using Grignard reagents).

Finally, we pursued accessing these polymers with functional chain-ends. Given that the polymerization is a Kumada CTP, terminal functionalization can be achieved by adding a monofunctional Grignard reagent. Indeed, end-capping was achieved with *o*-TolMgCl and vinyl magnesium chloride, as evidenced via MALDI-TOF Mass Spectrometry (see SI section IV.xi). These end-groups indicate that further diversity can be added to the chain-ends by using functionalized Grignard reagents (as demonstrated in previous CTP literature)[20] to install functional groups, or that the alkene can react by thiol-ene or Diels-Alder reactions to install small molecules or polymers.[31] We demonstrated this by preparing a pyridine functionalized grignard reagent (which can bind with Pd-SCS pincer complexes in solution)[32] and noted incorporation of pyridine end-groups onto the chain end of all polymers in solution via MALDI-TOF MS.

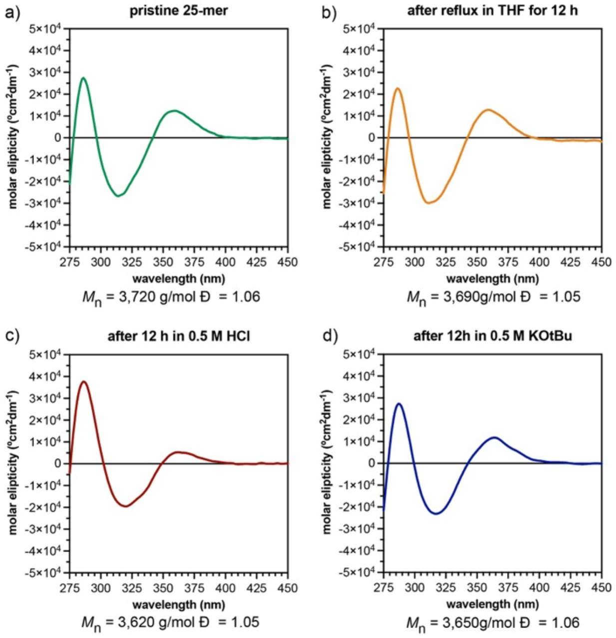


Figure 3. Solution-phase circular dichroism spectra of **P1$_{25}$** at 1 mg/mL in THF (a) before and (b) after reflux in THF for 12 hours; (c) stirring in 0.5 M HCl$_{(ether)}$ for 12 hours; (d) stirring in 0.5 M KO*t*-Bu$_{(THF)}$ for 12 hours.

In conclusion, we have developed a strategy to access functionalized, homochiral helical conjugated poly(thiophene)s via living catalyst-transfer polymerization. The polymers can be accessed with narrow dispersities (*Đ* < 1.10) and are stable to a variety of reaction conditions. We anticipate that the polymers described herein will be key building blocks in accessing functional polymers with structural hierarchy under a variety of conditions as well as in accessing biomimetic polymer catalysts or as materials for chemical separations. Additionally, because of the conjugated polymer structure, homochirality, and ordering of the side-chains, these polymers could have uses in optoelectronics or other organic electronic applications in which polymer chirality is important (such as in circularly polarized light generation)[33] or in applications where interactions between side-chains are important, such as in FRET or singlet fission applications.[34]

Supporting Information

Supporting Information – materials, synthetic procedures, and characterization. The authors have cited additional references within the Supporting Information.[35, 36, 37, 38, 39, 40, 41, 42]

Acknowledgements

The authors acknowledge financial support from the National Science Foundation under award number CHE 2203929. MDH acknowledges the Arnold and Mabel Beckman foundation for their generosity in providing a postdoctoral fellowship and research support. JAS thanks the DURF+ fellowship program at NYU for summer support. The authors also thank Prof. Tianning Diao and Dr. Jin Yang for use of the Diao lab's GC-FID.

Keywords: helical polymers, catalyst-transfer polymerization, homochirality, poly(thiophene)s

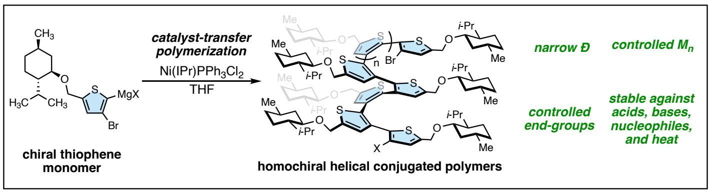
References

[1] A. Sali, E. Shakhnovich, M. Karplus, *Nature* **1994**, *369*, 248-251.
[2] W. S. Horne, T. N. Grossmann, *Nat. Chem.* **2020**, *12*, 331-337.
[3] P. D. Sun, C. E. Foster, J. C. Boyington, *Curr. Protoc. Protein Sci.* **2004**, *Chapter 17*, Unit 17 11.
[4] S. H. Gellman, *Acc. Chem. Res.* **1998**, *31*, 173-180.
[5] G. M. T. Huurne, A. R. A. Palmans, E. W. Meijer, *CCS Chemistry* **2019**, *1*, 64-82.
[6] R. E. Thompson, T. W. Muir, *Chem. Rev.* **2020**, *120*, 3051-3126.
[7] H. Frisch, B. T. Tuten, C. Barner‐Kowollik, *Isr. J. Chem.* **2020**, *60*, 86-99.
[8] G. Guichard, I. Huc, *Chem. Commun.* **2011**, *47*, 5933-5941.
[9] M. Milton, R. Deng, A. Mann, C. Wang, D. Tang, M. Weck, *Acc. Chem. Res.* **2021**, *54*, 2397-2408.
[10] E. Elacqua, K. B. Manning, D. S. Lye, S. K. Pomarico, F. Morgia, M. Weck, *J. Am. Chem. Soc.* **2017**, *139*, 12240-12250.
[11] E. Elacqua, G. T. Geberth, D. A. Vanden Bout, M. Weck, *Chem. Sci.* **2019**, *10*, 2144-2152.
[12] C. Wang, M. Weck, *Macromol. Rapid Commun.* **2021**, *42*, e2100368.
[13] C. Wang, A. Mann, M. D. Hannigan, R. H. Garvey, B. L. Dumlao, M. Weck, *Adv. Funct. Mater.* **2024**, *34,* 2313734.
[14] I. Song, J. Ahn, H. Ahn, S. H. Lee, J. Mei, N. A. Kotov, J. H. Oh, *Nature* **2023**, *617*, 92-99.
[15] J. Wade, J. N. Hilfiker, J. R. Brandt, L. Liiro-Peluso, L. Wan, X. Shi, F. Salerno, S. T. J. Ryan, S. Schoche, O. Arteaga, T. Javorfi, G. Siligardi, C. Wang, D. B. Amabilino, P. H. Beton, A. J. Campbell, M. J. Fuchter, *Nat. Commun.* **2020**, *11*, 6137.
[16] Z. Q. Wu, X. Song, Y. X. Li, L. Zhou, Y. Y. Zhu, Z. Chen, N. Liu, *Nat. Commun.* **2023**, *14*, 566.
[17] E. Yashima, K. Maeda, H. Iida, Y. Furusho, K. Nagai, *Chem. Rev.* **2009**, *109*, 6102-6211.
[18] B. Tilottama, K. Vijayakrishna, *Eur. Polym. J.* **2024**, *213*.
[19] A. K. Leone, A. J. McNeil, *Acc. Chem. Res.* **2016**, *49*, 2822-2831.
[20] J. P. Lutz, M. D. Hannigan, A. J. McNeil, *Coord. Chem. Rev.* **2018**, *376*, 225-247.
[21] H.-H. Zhang, C. Ma, P. V. Bonnesen, J. Zhu, B. G. Sumpter, J.-M. Y. Carrillo, P. Yin, Y. Wang, A.-P. Li, K. Hong, *Macromolecules* **2016**, *49*, 4691-4698.
[22] A. Yokoyama, R. Miyakoshi, T. Yokozawa, *Macromolecules* **2004**, *37*, 1169-1171.
[23] E. E. Sheina, J. S. Liu, M. C. Iovu, D. W. Laird, R. D. McCullough, *Macromolecules* **2004**, *37*, 3526-3528.
[24] A. K. Leone, P. K. Goldberg, A. J. McNeil, *J. Am. Chem. Soc.* **2018**, *140*, 7846-7850.
[25] T. Yokozawa, R. Suzuki, M. Nojima, Y. Ohta, A. Yokoyama, *Macromol. Rapid Commun.* **2011**, *32*, 801-806.
[26] L. Falivene, R. Credendino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, *Organometallics* **2016**, *35*, 2286-2293.
[27] R. Tkachov, V. Senkovskyy, H. Komber, A. Kiriy, *Macromolecules* **2011**, *44*, 2006-2015.
[28] K. Fujita, Y. Sumino, K. Ide, S. Tamba, K. Shono, J. Shen, T. Nishino, A. Mori, T. Yasuda, *Macromolecules* **2016**, *49*, 1259-1269.
[29] A. Yokoyama, A. Kato, R. Miyakoshi, T. Yokozawa, *Macromolecules* **2008**, *41*, 7271-7273.
[30] R. Miyakoshi, A. Yokoyama, T. Yokozawa, *Chem. Lett.* **2008**, *37*, 1022-1023.
[31] Z. Geng, J. J. Shin, Y. Xi, C. J. Hawker, *J. Polym. Sci.* **2021**, *59*, 963-1042.
[32] C. Wang, R. Deng, M. Weck, *Macromolecules* **2023**, *56*, 3507-3516.
[33] J. M. Moreno-Naranjo, F. Furlan, J. Wang, S. T. J. Ryan, T. Matulaitis, Z. Xu, Q. Zhang, L. Minion, M. Di Girolamo, T. Javorfi, G. Siligardi, J. Wade, N. Gasparini, E. Zysman-Colman, M. J. Fuchter, *Adv. Mater.* **2024**, *36*, e2402194.
[34] G. Lavarda, A. Sharma, M. Beslac, S. A. H. Jansen, S. C. J. Meskers, R. H. Friend, A. Rao, E. W. Meijer, *J. Am. Chem. Soc.* **2024**, *146*, 28985-28993.
[35] A. M. Borys, *Organometallics* **2023**, *42*, 182-196.
[36] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.
[37] A. W. H. Speed, E. N. Welsh, E. K. Burke, K. N. Robertson, *Synthesis* **2022**, *55*, 2406-2414.
[38] E. R. Curtis, M. D. Hannigan, A. K. Vitek, P. M. Zimmerman, *J. Phys. Chem. A* **2020**, *124*, 1480-1488.
[39] J. A. Bilbrey, S. K. Sontag, N. E. Huddleston, W. D. Allen, J. Locklin, *ACS Macro Lett* **2012**, *1*, 995-1000.
[40] S. Caddick, F. Geoffrey, N. Cloke, P. B. Hitchcock, J. Leonard, A. K. D. Lewis, D. McKerrecher, L. R. Titcomb, *Organometallics* **2002**, *21*, 4318-4319.

[41] T. Zell, P. Fischer, D. Schmidt, U. Radius, *Organometallics* **2012**, *31*, 5065-5073.

[42] F. Rey-Tarrio, R. Rodriguez, E. Quinoa, F. Freire, *Nat. Commun.* **2023**, *14*, 1742.

Entry for the Table of Contents



We report the synthesis of helical conjugated poly(thiophene)s via living catalyst-transfer polymerization. The polymers have narrow dispersities (Đ<1.10), can be accessed with controlled molecular weights (*n* = 10 – 100), and are stable in acids, bases, and strong nucleophiles. We envision these polymers will be useful in biomimetic and organic electronic applications due to the degree of control over the polymer structure and stability.

Institute and/or researcher Twitter usernames: @nyuchemistry, @nyumdi, @mattdhannigan