

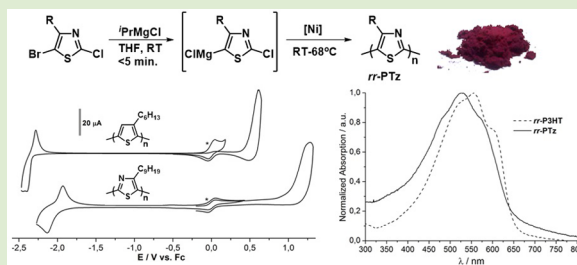
Head-to-Tail Regioregular Polythiazole Prepared via Kumada-Coupling Polycondensation

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S Supporting Information

ABSTRACT: Head-to-tail regioregular poly(4-alkylthiazoles) (C_9 -pTz, C_{13} -pTz, alkyl = n - C_6H_{19} , n - $C_{13}H_{27}$) have been synthesized and spectroscopically and electrochemically characterized. The pTzs were obtained by transmetalation of 2-chloro-5-bromo-4-alkylthiazoles with i PrMgCl, followed by Kumada-coupling polycondensation. The polymers are largely insoluble in organic solvents but dissolve readily in the presence of, e.g., trifluoroacetic acid (TFA). Analyses of soluble trace fractions of the polymers gave number average molecular weights (M_n) of 1.9–2.4 kDa (C_9 -pTz, PDI \approx 1.1–1.3) and 2.9–3.0 kDa (C_{13} -pTz, PDI \approx 1.1–1.2), as determined by gel permeation chromatography (GPC) relative to polystyrene standards, while the molecular weight of the bulk material is presumed to be considerably higher. Comparison of the 1H NMR spectra of the pTzs with a quaterthiazole model compound (4Tz) and head-to-head–tail-to-tail regioregular polybithiazole (PBTz) confirmed the head–tail structure and the high degree of regioregularity. The optical and electrochemical band gaps of C_9 -pTz were found to be similar to those of poly(3-hexylthiophene) (P3HT), while the frontier orbital levels are stabilized by 0.3–0.5 eV relative to those of the polythiophene. The synthesis of pTz via selective transmetalation of the precursor at the sterically hindered 5-position renders this synthesis a rare polycondensation of a *reversed* monomer. The implications for the polymerization mechanism are also discussed.

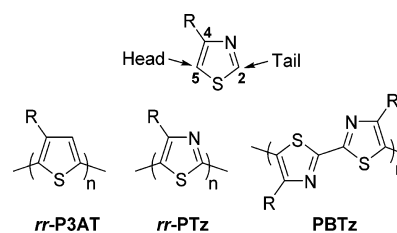


Conjugated polymers have been the subject of intense research throughout the past decades.¹ What makes these materials so desirable are the possible advantages they offer over inorganic semiconductors, namely, better processability and facile fine tuning of their properties by doping or modification of the monomers used. In recent years, a number of synthetic protocols for the polycondensation of in situ generated AB-bifunctional monomers via Kumada–Tamao- or Negishi-type cross-coupling reactions have been developed.² A number of electron-rich arenes, such as thiophene,^{3,4} selenophene,⁵ fluorene,⁶ carbazole,^{2b} pyrrole,⁷ dialkoxyphenylene,⁸ and thieno[3,4-*b*]pyrazine,⁹ have been polymerized via these methods. Efforts to synthesize potential n-type materials have so far been limited to the polymerization of pyridines,¹⁰ thiophenes with perfluoroalkyl side chains,¹¹ a dithienyl naphthalene diimide,^{12,10b} and a benzotriazole.¹³

The great potential of these preparative methods arises from the fact that living, chain-growth polycondensation behavior has been observed for a number of monomers. This process, then termed catalyst transfer polycondensation (CTP), furnishes well-defined polymers with low polydispersities and allows control over molecular weight and chain-end functionality.² Furthermore, CTP has been particularly successful in the synthesis of essentially 100% defect-free head-to-tail regioregular poly(3-alkylthiophene)s (*rr*-P3ATs, Chart 1).

In our group we are interested in further expanding the scope of CTP toward other electron-deficient building blocks, to access new potential n-type materials. In the line of this work

Chart 1



we have investigated thiazoles as substrates for Kumada-coupling polycondensation. Due to the electron-withdrawing imine functionality in the ring, thiazoles are comparatively electron deficient and have therefore been frequently employed as electron-accepting comonomers in conjugated oligomers and copolymers.^{14,15} Thiazole-based homopolymers, however, have received less attention in the literature.

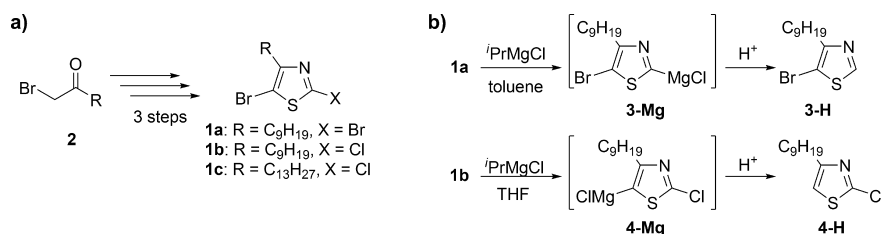
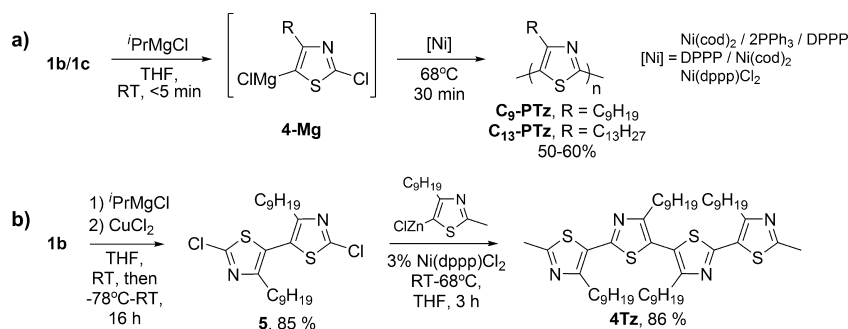
Yamamoto¹⁶ and Curtis¹⁷ published a series of works on head-to-head–tail-to-tail regioregular polybithiazoles (Chart 1, PBTz, R = Me, *n*-Bu, Ph, C_7H_{15} , C_9H_{19}) that were synthesized by dehalogenation polymerization of 5,5'-dibromo-2,2'-bithiazoles with equimolar amounts of Ni(0). A partially alkylated copolymer was prepared by Stille cross-coupling polycondensation.

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Scheme 1. (a) Monomer Synthesis and (b) Transmetalation Experiments

Scheme 2. Synthesis of (a) C_9 -PTz/ C_{13} -PTz and of (b) 4Tz

sation.^{16c} The only reports on the synthesis of actual polythiazole involved the Yamamoto polymerization of 2,5-dibromothiazoles that furnished regiorandom material with a head-to-tail content of ca. 30%.^{16c,d} In this work we present our results on the synthesis of head-to-tail regioregular poly(4-alkylthiazole)s (Chart 1, *rr*-PTz, R = *n*-C₉H₁₉, *n*-C₁₃H₂₇) via Kumada-coupling polycondensation of 2,5-dihalogenated 4-alkylthiazoles (**1a–c**).

As precursors for the planned polycondensation, 2,5-dihalogenated 4-alkylthiazoles were synthesized starting from α -halogenated ketones (**2**), as outlined in Scheme 1. 1-Bromoundecan-2-one (**2** (R = *n*-C₉H₁₉)) and 1-bromopentadecan-2-one (R = *n*-C₁₃H₂₆) were used to introduce the respective *n*-nonyl- and *n*-tridecyl groups in position 4 as solubilizing side chains. Several 2,5-dibromo-4-alkylthiazole derivatives (alkyl = Me, butyl, pentyl, heptyl, nonyl) have been previously employed in the synthesis of thiazole-containing polymers.¹⁵ Detailed preparative procedures for the monomer synthesis have also been included in the Supporting Information.

The 2,5-dibromothiazole **1a** and the 5-bromo-2-chloro-derivatives **1b** and **1c** were synthesized, and their behavior toward transmetalation with Grignard reagents was studied: Treatment of a solution of **1a** in toluene with ⁱPrMgCl·Et₂O leads to selective transmetalation at the 2-position, and the magnesio species **3-Mg** is formed (Scheme 1b, top). Conversion of the substrate is complete within minutes. However, while the resulting colloidal suspension of **3-Mg** in toluene is stable at ambient temperature, the intermediate was found to decompose rapidly in the presence of coordinating solvents (THF, Et₂O) and could therefore not be successfully employed in polymerization experiments. This issue does not arise with the 2-chloro-derivative **1b** (Scheme 2b, bottom). In this compound the reactivities of the 2- and 5-positions are reversed, and transmetalation with ⁱPrMgCl·Et₂O in THF exclusively furnishes the stable 5-metalated product **4-Mg**.

A comparison of the ¹H NMR spectra of the quenching products **3-H** and **4-H** confirms the alleged selectivity (see Figures S1 and S2 in the Supporting Information). The 2-CH

group in **3-H** yields a singlet at 8.70 ppm, while the proton in the 5-position of **4-H** is observed at 6.76 ppm. Both signals lie in the typical range expected for the respective ring positions in 1,3-thiazoles.¹⁸

In a typical polymerization experiment, **1b** or **1c** was transmetalated with 0.95 or 1.0 equiv of ⁱPrMgCl·Et₂O in THF, and the reaction mixture was heated to reflux. A Ni(0)- or Ni(II)-precatalyst was added to the refluxing solution, and the reaction mixture was heated for 30 min (Scheme 2a, for details see methods A, B, and C in the Supporting Information). The precipitated polymer was then isolated by washing on a Soxhlet (MeOH, acetone), followed by extraction with chloroform and chlorobenzene (ca. 1% yield each) and recovery of the insoluble bulk material (50–60%).

The bulk material of the obtained poly(4-nonylthiazole) (**C**₉-PTz) and poly(4-tridecylthiazole) (**C**₁₃-PTz) showed virtually identical UV–vis and NMR spectra (see Figures S3 and S4 in the Supporting Information), indicative of identical regiostructures in both polymers. Analysis of the chloroform-soluble fractions **C**₉-PTz_{CF} and **C**₁₃-PTz_{CF} via GPC consistently gave number-average molecular weights of *M*_n = 1.9–2.4 kDa (PDI ≈ 1.1–1.3, DP = 8.4–11.4)¹⁹ for **C**₉-PTz and *M*_n = 2.9–3.0 kDa (PDI ≈ 1.1–1.2, DP = 10.9–11.3) for **C**₁₃-PTz. In both cases, the molecular weight of the insoluble bulk fraction is presumed to be considerably higher.

The bulk polymer fractions dissolve in hot 1-chloronaphthalene (**C**₉-PTz) or hot 1,2,4-trichlorobenzene (**C**₁₃-PTz) while being insoluble, e.g., in boiling *ortho*-dichlorobenzene, α,α,α -trifluorotoluene, anisole, DMF, and acetic acid. However, the polymers dissolve readily in chloroform in the presence of strong proton or Lewis acids like trifluoroacetic acid (TFA) or boron trifluoride. A preliminary analysis of the bulk **C**₉-PTz via GPC in CF/TFA relative to different batches of **PBTz** of known molecular weight²⁰ confirmed the increased molecular weight: Bulk **C**₉-PTz showed a significantly greater retention time than both **C**₉-PTz_{CF} and the lowest MW batch of **PBTz** (*M*_n = 3.0 kDa, PDI 1.46, see Figure S5 in the Supporting Information). Given the indirect nature of this method and the

broad polydispersities of the employed PBTz references, a more concrete estimate cannot be made at this point.

To confirm the regio-structure of the polymer, an oligomeric model compound that mimics *rr*-PTz was also synthesized (Scheme 2b). Selective transmetalation of **1b** at the 5-position, followed by copper-mediated oxidative coupling, gave the head-to-head-coupled 2,2'-dichloro-4,4'-dinonyl-5,5'-bithiazole (**5**). Negishi coupling of this building block with 2 equiv of a 4-nonyl-5-zincothiazole then furnished the model thiazole **4Tz** that was completely characterized via NMR, high-resolution mass spectroscopy, and elemental analysis.

In the ^1H NMR spectrum of $\text{C}_9\text{-PTz}$ in $\text{CDCl}_3/\text{TFA-}d_1$, the α -methylene groups of the alkyl chains show a distinct signal centered at 3.19 ppm, while for PBTz the corresponding peak is observed at 2.82 ppm in the same solvent mixture (Figure 1).

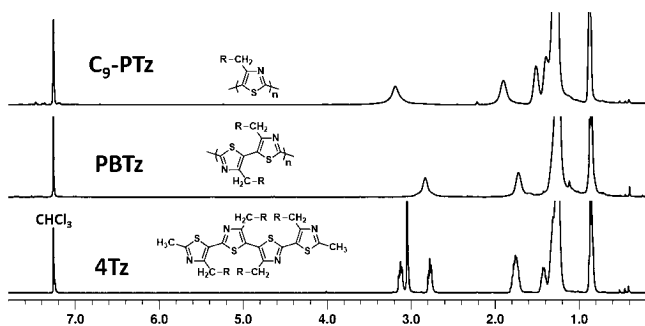


Figure 1. Comparison of ^1H NMR spectra of $\text{C}_9\text{-PTz}$, PBTz, and **4Tz**. Spectra recorded in CDCl_3 containing 10 vol. % $\text{TFA-}d_1$. $\text{R} = \text{C}_8\text{H}_{17}$.

For **4Tz** two separate triplets are observed at 3.13 ppm ($^3J_{\text{HH}} = 8.0$ Hz) and 2.78 ppm ($^3J_{\text{HH}} = 7.7$ Hz), while the signal of the terminal CH_3 groups appears as a singlet at 3.06 ppm.

The good agreement between the spectra of **4Tz** and respective signals of both $\text{C}_9\text{-PTz}$ and PBTz provides convincing evidence for a highly regioregular head-to-tail structure in $\text{C}_9\text{-PTz}$. Within the accuracy of the ^1H NMR experiment ($\approx 5\%$) no head-to-head coupling defects could be detected in the bulk material. The electronic properties of the polymers were then characterized and were found to be very similar for $\text{C}_9\text{-PTz}$ and $\text{C}_{13}\text{-PTz}$. In the following, only the analytical data for $\text{C}_9\text{-PTz}$ will therefore be reported (Figures 2a and 2b). To provide a consistent frame of reference, the properties of both of PBTz and P3HT were also measured under similar conditions.

The UV-vis absorption spectrum of a thin film of $\text{C}_9\text{-PTz}$ drop cast from hot 1-chloronaphthalene showed weak vibronic structuring with an absorption maximum at 526 nm and an absorption onset at ca. 655 nm (Figure 2a). Thin films of PBTz and P3HT show similar absorption onsets corresponding to optical band gaps of ca. 1.9 eV, in agreement with the literature.¹⁷ The absorption spectrum of soluble $\text{C}_9\text{-PTz}_{\text{CF}}$ is shifted to significantly shorter wavelengths with a λ_{max} of 450 nm and an absorption onset observed at ca. 620 nm (2.00 eV). This indicates a significantly lower molecular weight or possibly the presence of regiodefects in this fraction of the polymer.

We further investigated thin films of $\text{C}_9\text{-PTz}$ via cyclic voltammetry (Figure 2b). The insolubility of the polymer required preparation of the electrodes by rub-coating, rather than the usual dip-coating process. The experiments were carried out in acetonitrile with 0.1 M $[\text{NnBu}_4][\text{PF}_6]$ as supporting electrolyte at a scan rate of 50 mV/min. Reference

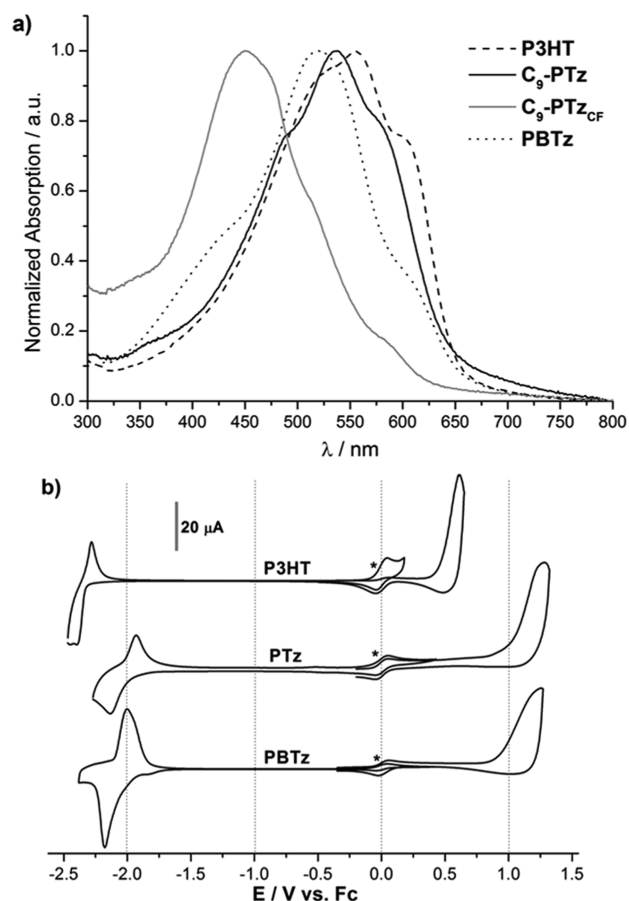


Figure 2. (a) Thin-film UV-vis absorption spectra of P3HT, $\text{C}_9\text{-PTz}$, $\text{C}_9\text{-PTz}_{\text{CF}}$, and PBTz. $\text{C}_9\text{-PTz}$ and PBTz films were drop-cast from 1-chloronaphthalene. P3HT and $\text{C}_9\text{-PTz}_{\text{CF}}$ were spin-coated from chloroform. (b) Cyclic voltammograms of P3HT, $\text{C}_9\text{-PTz}$, and PBTz. Recorded as rub-coated films in acetonitrile and 0.1 M $[\text{NnBu}_4][\text{PF}_6]$ at 50 mV/s. * = Fc/Fc^+ standard.

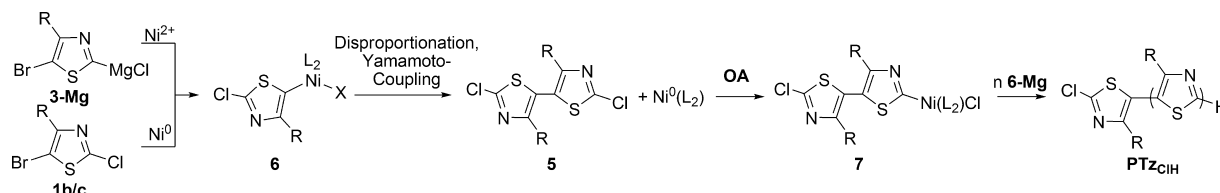
Table 1. Physicochemical Data for $\text{C}_9\text{-PTz}$, PBTz, and P3HT

polymer	$E_{1/2}^{\text{red}}$ (V)	$E_{\text{g}}^{\text{opt}\alpha}$ (V)	E_{g}^{CV} (V)	HOMO (eV) ^b	LUMO ^{opt} (eV) ^c
$\text{C}_9\text{-PTz}$	-2.09	1.90	2.91	-6.10	-4.20
PBTz	-2.03	1.90	2.85	-6.03	-4.13
P3HT	-2.34	1.90	2.77	-5.55	-3.65

^aDerived from the absorption onset of thin-film UV-vis spectra. ^bRelative to the HOMO of ferrocene (-5.1 eV).²¹ ^cDerived from the electrochemical HOMO and the optical band gap.

data for PBTz and P3HT were recorded under the same experimental conditions, and the electrodes were prepared in the same fashion. PBTz and $\text{C}_9\text{-PTz}$ exhibit comparable oxidation and reduction potentials. Both polymers undergo fully reversible reduction with half potentials of $E_{1/2}^{\text{red}} = -2.09$ V and $E_{1/2}^{\text{red}} = -2.03$ V, respectively, relative to ferrocene. The reduction potentials are therefore shifted to higher potential by ca. 0.3 V relative to P3HT ($E_{1/2}^{\text{red}} = -2.34$ V) under the same conditions. The polythiazole films were stable over multiple reduction/reoxidation cycles (>15), while oxidation was either irreversible or possibly led to degradation of the film. Oxidation onsets at +0.93 V and +1.00 V relative to the ferrocene standard were observed, shifted by ca. 0.5 V relative to P3HT. On the basis of these data, the energy levels for the highest occupied molecular orbitals (HOMOs) and the lowest

Scheme 3. Initiation Pathway for the Polymerization of 1b/1c



unoccupied molecular orbitals (LUMOs) were calculated, as summarized in Table 1 (see also Table S1 in the Supporting Information). A comparatively large difference between the optical and electrochemical band gaps was observed ($\Delta E \approx 0.9\text{--}1.0\text{ V}$). Since this difference was consistently found for all three samples, including P3HT, we attribute this to the way the polymer films were prepared.

It has to be pointed out that the transmetalation product **4-Mg** is a “reversed” monomer, metalated at the sterically hindered 5-position, as opposed to a “regular” monomer that is metalated at the sterically unhindered position, farthest from the side chain (as in the case of **3-Mg**, Scheme 1b). The initiation pathways of these different types of monomers are crucially different, which also affects the polymerization process.^{2a,d,4a}

Generally, the polymerization can be performed by adding either a solution of a Ni(0)-precursor or a suspension of $\text{Ni}(\text{dppp})\text{Cl}_2$ to a refluxing solution of **4-Mg** in THF. When a Ni(0)-precursor is used, the presence of residual **1b/c** in solution is required. Our current analytical data indicate that the head-to-head-coupled dimer **5** is initially formed via Yamamoto coupling of the monoaryl complex **6** (Scheme 3). Oxidative addition of **5** onto the concurrently generated Ni(0) then furnishes complex **7** from which the polymerization can proceed. This process should furnish a Cl/H-terminated polymer (PTz_{C1H}) containing one head-to-head defect. The viability of this mechanism was corroborated by MALDI-MS data that showed the almost exclusive formation of H/Cl- and Cl/Cl-terminated polymer species (see Figures S6 and S7 in the Supporting Information). Furthermore, when **1b/c** is reacted with an equimolar amount of Ni(0), oligomeric products are formed under mild conditions that predominantly contain head-to-head linkages (see Figure S8 and associated comments in the Supporting Information). This latter finding clearly shows that the proposed initiation pathway can readily be entered. Still, the number of head-to-head defects in the bulk material remains below the detectable limit (<5%, see also Figure S4 in the Supporting Information) even at very high catalyst loading. It is therefore unlikely that Yamamoto coupling occurs during the extension of the polymer chains.

In conclusion, we have synthesized poly(4-alkylthiazole) via Kumada-coupling polycondensation of *reversed* monomers. Highly head-to-tail regioregular material with a number-averaged molecular weight significantly greater than 3.0 kDa was obtained, and its head-to-tail regiostructure was confirmed. C₉-PTz and its regioisomer PBTz exhibit electrochemical and optical band gaps that are comparable to P3HT, while their frontier orbitals are stabilized by ca. 0.3–0.5 eV relative to those of the polythiophene. Preliminary findings indicate that the initiation mechanism for the polycondensation of *reversed* AB-bifunctional monomers is crucially different from the one for *regular* monomers. A more detailed study of the polycondensation process will be performed, when thiazole derivatives with better solubilizing side chains are made available.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and additional analytical data are supplied. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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