Macromolecules

Soluble Head-to-Tail Regioregular Polythiazoles: Preparation, Properties, and Evidence for Chain-Growth Behavior in the Synthesis via Kumada-Coupling Polycondensation

Frank Pammer,*^{,†} Jakob Jäger,[†] Benjamin Rudolf,[†] and Yu Sun[‡]

[†]Institute of Organic Chemistry II and Advanced Materials, University of Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany [‡]Fachbereich Chemie, TU Kaiserslautern, Erwin-Schrödinger-Strasse 54, D-67663 Kaiserslautern, Germany

Supporting Information

ABSTRACT: Head-to-tail regioregular poly(4-alkylthiazole)s containing silylethers in the side-chains were synthesized via Kumada-Coupling polycondensation of "*reversed*" monomers, that were metalated at the sterically hindered 5-position. Their optical, electrochemical, and bulk properties have been studied, and evidence is presented that indicates the occurrence of quasi-living chain-growth behavior in the polymerization process. Two polymers, **PTzTIP** and **PTzDIBO**, featuring triisopropylsilyl and diisobutyloctadecylsilyl side chains, respectively, were prepared. **PTzTIP** is largely insoluble, while **PTzDIBO** is fully soluble in common organic solvents, including hexane, and readily gave number-averaged molecular weights exceeding 100 kDa, corresponding to an average degree of polymerization greater than 200, as determined via gel-permeation chromatography (GPC) in CHCl₃. The formation of



a regular head-to-tail regiostructure could be confirmed through comparison with a head-to-head-tail-to-tail regioregular polybithiazole (**PBTzTIP**), synthesized via Yamamoto-polymerization of a head-to-head-linked bithiazole. Regioregular **PTzDIBO** could be obtained via different polymerization protocols, including external initiation with two new aryl-nickel-complexes, which furnished material with particularly low polydispersities (<1.4 at $M_n > 100$ kDa). Furthermore, a direct correlation between the obtained molecular weight and the monomer/catalyst ratio was observed in series of batch polymerization experiments, in agreement with a chain-growth polycondensation process. The incorporation of the precatalyst–aryl moiety into the polymer chains could be proven by comparison with a model compound. The functionalized end-groups allowed to independently determine the molecular weight via ¹H NMR, which gave good agreement with the values obtained from GPC, further corroborating the occurrence of chain-growth.

INTRODUCTION

Conjugated polymers have been the subject of intense research in the last decades.¹ Polythiophenes (**PT**s) in particular are among the most intensely studied polymeric semiconductors, and have been widely employed in the fabrication of organic electronic devices, such as organic field effect transistors, organic light-emitting diodes, and organic photovoltaic cells.² Also, functionalized **PT**s played important roles in conjugated polymer-based sensors.³

The regioregularity of poly(3-alkylthiophenes) (*rr*-P3ATs, Chart 1) has been shown to critically affect the materials properties, including the optical band gap and the electrical conductivity after doping. A coplanar arrangement of the thiophene rings in *rr*-P3ATs generally results in a larger effective conjugation length, and allows for aggregation via π -stacking in the solid state which in turn is beneficial for charge carrier mobility and overall performance of organic electronic devices. For the preparation of highly regioregular *rr*-P3ATs and other polyarenes, polymerization protocols summarized under the term catalyst transfer polycondensation (CTP) have recently emerged as the method of choice.⁴ CTP protocols allow for the controlled chain-growth polycondensation of AB-bifunctional arenes, and primarily involve the cross-coupling of *in situ* generated Grignard and organozinc species, with nickel catalysts. Recently, chain-growth polycondensation of via Suzuki-coupling has also been reported.^{5,4b} Quasi-living chain-growth behavior could be observed for a number of electron-rich polyarenes, such as *rr*-P3ATs,⁶ polyselenophene,⁷ polyfluorene,⁸ polypyrrole,⁹ and poly(dialkoxyphenylene).¹⁰ More electron-deficient polymers, on the other hand, have been investigated to a much lesser degree. Chain-growth behavior was observed in the synthesis of polypyridines,¹¹ a naphthalene diimide—bithiophene copolymer,¹² and a poly(benzotriazole).¹³ Polythiophene bearing perfluoro-alkyl side-chains,¹⁴ and poly(thieno[3,4-*b*]pyrazine¹⁵ could also be synthesized via Kumada- and Negishi-type polycondensations,

Received: June 12, 2014 Revised: August 6, 2014 Chart 1



respectively, but the occurrence of chain-growth was not reported.

In our group we are interested in further expanding the scope of CTP toward more electron-deficient heterocyclic building blocks, in order to access new potential n-type materials. To this end, we recently explored the synthesis and properties regioregular poly(4-alkylthiazole)s (*rr*-**PTzs**, Chart 1) via CTP. While thiazoles are isoelectronic to thiophenes, the electronwithdrawing imine-nitrogen in the ring renders them comparatively electron-poor. Accordingly, partial substitution, of thiophene against thiazole in an otherwise head-to-tail regioregular P3AT (**PTTz**, **PTTTz**, Chart 1) leads to increasing stabilization of the frontier orbitals.¹⁶ The potential of thiazoles in the fabrication of n-type materials has been demonstrated,

Scheme 1. Monomer Synthesis and Polymerization Experiments

e.g., by Yamashita et al., who reported oligo-thiazole based nchannel organic field effect transistors (OFETs) that exhibited electron mobilities exceeding 1 cm²/(V s) and required a lowered threshold voltage compared to their thiophene analogues.¹⁷ Thiazole and thiazole derivatives have been frequently employed as electron-accepting comonomers in conjugated polymers.^{18,19} Reports on thiazole homopolymers, however, are largely limited to works by Yamamoto²⁰ and Curtis²¹ on the properties of headto-head-tail-to-tail regioregular polybithiazoles (**PBTz**, Chart 1).

Recently, we were able to report the synthesis and properties of head-to-tail regioregular polythiazoles bearing *n*-alkyl-chains in the 4-position (Chart 1, C₉-PTz: R = n-C₉H₁₉, C₁₃-PTz: R = n-C₁₃H₂₇).²² In agreement with the properties of PTTz/ PTTTz,¹⁶ the investigated *rr*-PTzs exhibited optical and electronic band gaps comparable to *rr*-P3ATs, while their frontier orbitals levels were stabilized by ca. 0.3–0.5 eV. Unfortunately, C₉-PTz and C₁₃-PTz were largely insoluble in organic solvents. The molecular weight of the bulk material could therefore not be determined, and the polymerization process could not be investigated in detail.

Herein, we report the synthesis of 2,5-dihalogenated thiazoles (1a/b, Scheme 1) with silyloxymethyl-side-chains that furnish better soluble polythiazoles (PTzTIP, PTzDIBO, Chart 1). Their properties are discussed and evidence is presented for the occurrence of a chain-growth process in the polymer synthesis via nickel-catalyzed Kumada-coupling polycondensation.

RESULTS AND DISCUSSION

Monomer and Polymer Synthesis. The monomers were obtained via a five-step synthesis, as outlined in Scheme 1. Starting from 1-bromoethylpyruvate (2) the thiazole ring was built up (3), and was halogenated (4, 5), followed by conversion of the carboxylic acid ester 5 to the corresponding thiazolylalcohol 6. The alcohol was then reacted with trialkylchlorosilanes



in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to furnish the corresponding silylethers featuring triisopropyl- (1a) and diisobutyloctadecylsilyl groups (1b). Analogous to our previous report, treatment of 1a/b with 'PrMgCl leads to quantitative metalation at the 5-position, and the corresponding AB-bifunctional Grignard species 7-Mg_{a/b} are formed (Scheme 1b, Figure 1). Treatment of 7-Mg_a with copper(II) chloride results



Figure 1. $^1\mathrm{H}$ NMR spectra of (a) hydrolyzed 7-Mga and (b) 1a in CDCl_3.

in oxidative homocoupling and formation of the head-to-headcoupled 2,2'-dichloro-5,5'-bithiazole 8 (Scheme 1c). Yamamoto-polymerization of 8 yields the head-to-head-tailto-tail regioregular polybithiazole **PBTzTIP** ($M_n = 5.9$ kDa, PDI = 2.06), which served as reference material to corroborate the regioregularity of **PTzTIP** and **PTzDIBO**.

Polymerization of $7\text{-}Mg_{a/b}$ could be performed according to different preparative protocols (methods A through C in the Supporting Information) with Ni(dppe)- or Ni(dppp)-based catalysts (dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3bis(diphenylphosphino)propane), which furnished the polymers PTzTIP and PTzDIBO, respectively, as bright orange fluorescent solids. However, the bulk of PTzTIP was found to be soluble only in high boiling haloarenes such as hot 1,2-dichlorobenzene (ODCB) or 1,2,4-trichlorobenzene. The chloroformsoluble trace fractions of PTzTIP gave maximum numberaveraged molecular weight of $M_{\rm p} = 2.7$ kDa (PDI = 1.30, DP_p \approx 10-11), while the molecular weight of the insoluble bulk material is presumed to be higher. PTzDIBO, on the other hand, is fully soluble in common organic solvents, including hexane, and readily gave molecular weights exceeding 100 kDa ($DP_n > 200$), as determined via GPC relative to polystyrene standards.²³⁻²⁵ Unless stated otherwise, analytical studies reported in the following have been carried out with the insoluble bulk material of PTzTIP, synthesized with a Ni(cod)₂/dppp-catalyst system (method B in the Supporting Information, cod =1,5-cyclooctadiene), and with two batches of PTzDIBO with number-average molecular weights of 111.6 kDa (PDI = 2.13), and 93.0 kDa (PDI = 2.19), that were synthesized with Ni(dppp)Cl₂ (method A in the Supporting Information) and Ni(cod)₂/dppp as catalyst, respectively. The polymerization proceeds quickly, and was generally complete within 40 min even when carried out at 0 °C (see Figures S3 and S4 in the Supporting Information). The high reaction speed is insofar surprising as a formally less reactive aryl chloride is employed. The lower reactivity seems offset, however, by the known high reactivity of the 2-position of the thiazole ring.²⁶ Furthermore, nickel is generally more active in the crosscoupling of aryl chlorides compared to palladium.²⁷

Regiostructure. The head-to-tail structure of the polymers can be inferred from the characteristic chemical shift of the benzylic α -methylene group (TzCH₂OSiR₃, Figure 2A).²⁸ In ¹H NMR spectra of **PTzDIBO** and **PTzTIP** recorded in



Figure 2. (A) ¹H NMR spectra of polythiazoles recorded in 1,2dichlorobenzene-d₄ (ODCB-d₄) at 100 °C (**PTzDIBO**, **PBTzTIP**) and at 150 °C (**PTzTIP**). * = end groups and low molecular weight oligomers. (B) Close-up of the peak of **PTzDIBO** (M_n = 93.0 kDa) at 100 °C in ODCB-d₄.

ODCB- d_4 at 100 and 150 °C, respectively, the corresponding signals are observed at 5.27 and 5.28 ppm. The corresponding signal in the head-to-head-tail-to-tail regioregular PBTzTIP appears at 5.00 ppm in the same solvent. This signal offset is similar but somewhat smaller than the one previously reported for head-to-head- and head-to-tail-dyads of oligo- and poly-(4-alkylthiazole)s (ca. 0.4 ppm).²² A close-up of the signal of high molecular weight PTzDIBO (Figure 2B, see also and Figures S30 and S33 in the Supporting Information) shows only trace signals associated with possible head-to-head-defects. While this indicates a high degree of regioregularity, tail-to-tail-defects may still be present. Signals associated with inherent regio-defects can be unambiguously observed only in lower molecular weight samples $(M_{\rm p} < 15 \text{ kDa}, \text{ e.g.}, \text{ Figure 7c})$. Here two individual peaks can be resolved at 5.09 and 5.11 ppm (recorded at 50 °C in CDCl₃), that can be observed as a shoulder only for higher molecular weight samples. Since the minor signal is not detectable in high molecular weight samples, we tentatively attribute it to chain-end dyads. However, it may also be associated with regio-defects generated in the initiation steps. The regioregularity of PTzDIBO can also be inferred from ¹³C NMR data that shows four wellresolved signals for the thiazole ring and the α -methylene-group at 157.0, 154.7, 131.7, and 60.0 ppm (Figure S34 in the Supporting Information). Extensive regio-defects are expected to lead to multiple signals in the ¹³C NMR,²⁹ or cause severe signal broadening.

Optical and Electronic Properties. The electronic properties of PTzDIBO and PTzTIP have been studied via UV-visand fluorescence spectroscopy. For brevity only the properties of PTzDIBO will be discussed. In THF solution PTzDIBO exhibits a longest wavelength absorption maximum (λ_{max}) at 503 nm and an absorption onset at 568 nm. In absorption spectra of thin films, spin coated from THF, the main absorption maximum exhibits a marginal blueshift to 502 nm, and new maximum emerges at 533 nm along with a concurrent shift of the absorption onset to 590 nm, corresponding to an optical band gap of 2.10 eV. Annealing of the film of PTzDIBO at up to 120 °C did not alter the absorption spectrum, while upon annealing above 140 °C the maximum at 533 nm is reduced to a shoulder band, and a new shoulder centered on ca. 477 nm emerges (see Figures S5 through S7 in the Supporting Information). Overall, only a minor bathochromic shift of the absorption onset is observed, when moving from solution to the solid state. This is in contrast to the optical properties of

rr-P3ATs² and recently reported PTTz/PTTTz¹⁶ that exhibit substantial bathochromic shifts in the film compared to spectra recorded in solution. The bathochromic shift is associated with $\pi - \pi$ stacking of the conjugated polymer backbone, and is generally more pronounced for regioregular polymers than for random polymers containing regio-defects.^{2,31} In the present case, however, the limited bathochromic shift is attributed to the bulk of the side-chains preventing aggregation, rather than to the presence of regio-defects. PTzDIBO fluoresces with a quantum vield of 26% in THF solution; within the same range commonly observed for regioregular polythiophenes.³² The emission spectrum in solution revealed only a narrow Stokes shift and well-defined vibronic structuring. In solution emission maxima are observed at 550 and 590 nm along with two additional shoulder bands. Fluorescence also persists in the thin film, although the 550 nm transition is not observed and the vibronic structure is less pronounced. The marginal Stokes shift and the vibronic structuring indicate a rigid conformation of the conjugated polymer backbone of PTzDIBO in solution. Indeed, the vibronic structuring is more pronounced than what is observed for *rr*-P3HT,^{33,32} but rather reassembles more rigid conjugated π -systems that contain, e.g., fluorene³⁴ or ladder-type polymer structures.³⁵ This observation may be explained by a recent report by Bronstein and co-workers who demonstrated that a coplanar conformation of head-to-tail-linked thienylthiazole-dyads is stabilized through interaction of the lone pair on nitrogen with the antibonding σ^* -orbitals of the C–S-bonds in the adjacent ring.¹⁶ In order to substantiate the presence of this stabilizing interaction in thiazole-homopolymers, the above calculation has been reproduced with in a head-to-tail-linked bithiazole-dyad (see section 1.3 in the Supporting Information for details). The calculations showed the rotational barrier in a bithiazole-dyad to be very close in energy to the one previously reported for thienyl-thiazole, and substantially greater what is found for bithiophenes. Other researchers have reported O…Sbased weak interactions to also promote a coplanar conformation of adjacent rings in conjugated polymers, and to thereby affect the bulk morphology of the material.³⁶ However, while the stabilizing interaction clearly affects the electronic properties of PTzDIBO in solution, a possible influence on the solid state morphology of *rr*-PTzs still remains to be established.

Analyses of PTzTIP and PTzDIBO via cyclic voltammetry showed the two polymers to have very similar electrochemical properties (Figure 3b, Table 1). For reference purposes, previously reported electrochemical data for rr-P3HT, PBTz, and Co-PTz, recorded under similar experimental conditions, are also included in Table 1.22 Both PTzTIP and PTzDIBO undergo quasi-reversible reduction while oxidation was irreversible with oxidation-onsets observed at +0.95 and +0.99 V relative to the ferrocene/ferrocenium redox couple (Fc/Fc^+) . These latter values are very close to those previously observed for C₉-PTz and PBTz, and correspond to energy levels for the highest occupied molecular orbitals (HOMO) of -6.05 eV for PTzTIP and -6.09 eV for PTzDIBO, based on the HOMO of ferrocene (-5.10 eV).³⁹ The onsets of the reduction waves at -1.69 V and -1.74 V lead to electrochemical band gaps of 2.64 eV (PTzTIP) and 2.73 eV (PTzDIBO). The difference between the electrochemical and optical band gaps of the polymers reported herein (ca. 0.6 V) is significantly less than what was observed for C_9 -PTz and PBTz (0.9-1.0 V).² As a consequence, the energy levels for the lowest unoccupied molecular orbitals (LUMO) of PTzTIP and PTzDIBO derived from the electrochemical and optical band gaps either appear



Figure 3. (a) UV–vis absorption- and fluorescence-spectra **PTzDIBO** in THF solution and as thin film. Absorption spectrum in solution recorded at 19.8 μ g/mL, fluorescence spectrum recorded at 0.5 μ g/mL. (b) Cyclic voltammograms of **PTzDIBO** and **PTzTIP**. Recorded as rub-coated films in acetonitrile, 0.1 M [N*n*Bu₄][PF₆] at 50 mV/s. * = Fc/Fc⁺ standard.

to be stabilized (electrochemical, LUMO^{CV}) or destabilized (optical, LUMO^{opt}), compared to C_9 -PTz and PBTz. In a study on the properties of regioregular poly[3-(*n*-butyloxymethyl)-thiophene] (P3MBT) Zoombelt and co-workers found that the introction of alkoxymethyl-groups does not affect the frontier orbital levels of the polymer compared to P3HT.³⁷ In agreement with this finding, the HOMO-levels of all reported polythiazoles are virtually identical. Hence, the differences in LUMO-levels are rather attributed to packing effects in the solid state and the quasi-reversible nature of the electrochemical reductions observed for PTzTIP and PTzDIBO.

Thermal Analyses and Solid State Properties. Thermal analyses were carried out on PTzTIP and PTzDIBO, as well as on the previously reported polymers C_{13} -PTz and C_{9} -PTz (see Figures S8 and S9 in the Supporting Information). Thermogravimetric analyses (TGA) showed C₁₃-PTz and C₉-PTz to be equally thermally robust up to 440 °C, where rapid degradation sets in. The silvloxy-substituted polymers were found to be somewhat less durable and decomposed above 410 $^\circ$ C. In differential scanning calorimetry (DSC) C₉-PTz was found to decompose without melting, while melting of PTzTIP set in at ca. 425 °C but appeared irreversible due to concurrent decomposition. In contrast, C_{13} -PTz exhibited a melt endotherm at 386 °C upon heating, complemented by a crystallization exotherm at 362 °C in the cooling cycle, while for PTzDIBO a reversible phase transition was observed with a melting endotherm at 145 °C upon heating and a sharp crystallization exotherm at 140 °C (scan rate 20 °C/min). No phase transitions

Table	1. Electroc	hemical	Potentials	Given i	n V	Relative	to	Fc/Fc ⁺	with	Orbital	Energies	Given in o	eV
-------	-------------	---------	------------	---------	-----	----------	----	--------------------	------	---------	----------	------------	----

polymer	$E_{ m onset}^{ m red}$	$E_{\text{onset}}^{\text{ox}}$	$E_{1/2}^{\mathrm{red}}$	$E_{g}^{\text{opt }a}$	E_{g}^{CV}	HOMO ^b	LUMO ^{opt b}	LUMO ^{CV b}
C_9 -PTz ^c	-1.91	1.00	-2.09	1.90	2.91	-6.10	-4.20	-3.19
PBTz ^c	-1.92	0.93	-2.03	1.90	2.85	-6.03	-4.13	-3.18
rr-P3HT ^c	-2.32	0.45	-2.34	1.90	2.77	-5.55	-3.65	-2.78
PTzTIP	-1.69	0.95	d	2.09	2.64	-6.05	-3.96	-3.41
PTzDIBO	-1.74	0.99	d	2.10	2.73	-6.09	-3.99	-3.36

^{*a*}Derived from the absorption onset of the thin film UV–vis spectra. ^{*b*}Derived from the oxidation onset and the HOMO-energy of ferrocene (–5.10 eV), and the optical (LUMO^{opt}) and electrochemical (LUMO^{CV}) band gaps.³⁸ ^{*c*}Data adapted from ref 22. ^{*d*}**PTzTIP** and **PTzDIBO** showed only quasi-reversible reduction waves.

could be observed for **PTzDIBO** at higher temperatures. The higher temperature melting events observed for **PTzTIP** and C_{13} -**PTz** are attributed to melting of the polymer main-chain, while the reversible phase transition observed for **PTzDIBO** is rather associated with melting of the side-chains.

In order to further elucidate the structures of the polymers in the solid state, samples of C9-PTz, C13-PTz, PTzTIP, and PTzDIBO have been investigated via wide-angle X-ray scattering (WAXS). The refractograms of C9-PTz and C13-PTz (Figure 4, A1/A2) are dominated by broad peaks centered on ca. 25° and 20°, corresponding to distances of ca. 3.7 and 4.7 Å, attributed to the densely π -stacked polymer backbone,^{31,21b} and amorphous regions,^{21b} respectively. PTzTIP shows a significantly different refraction pattern that becomes better resolved upon prolonged heating of a suspension of the polymer in chlorobenzene (Figure 4, B1/B2). Maxima associated with π -stacking at 23.2° and 24.8° (3.9 and 3.7 Å) are present. Still, the most prominent features are maxima at 13.6°, 14.9°, and 16.5° (6.6, 6.0, and 5.4 Å), that do not correspond to a readily identifiable repeat-structure in the polymer. PTzDIBO exhibits an again altered refraction pattern (Figure 4, C1/C2). In the refractogram of a compacted pellet prominent peaks are visible at 14.5°, 20.7° and 21.5° (6.2, 4.4, and 4.2 Å), along with other signals (Figure 4, C1). Heating of the polymer to 150 °C, followed by slow cooling led to partial crystallization of the sample and gave a better resolved refractogram (Figure 4, C2). The signals observed in the original sample are still present at 14.6°, 20.7° and 21.7° (6.2, 4.4 and 4.2 Å). The peak at 14.6° may be associated with the side-chain-repeat height,³¹ while the peaks at 20.7° and 21.7° most likely correspond to densely packed alkyl chains.³⁸ A peak at 25.5° (3.6 Å), that may be associated with π -stacking also emerges in the crystallized sample.

These findings indicate, that in the insoluble polymers C₉-**PTz**, C₁₃-**PTz** extensive π -stacking is prevalent, while due to the increased bulk of the side-chains in **PTzTIP** π -interactions are less predominant. The solid state structure of **PTzDIBO**, on the other hand, appears to be dominated by the packing of the octadecyl-side-chains, which is corroborated by the low melting point and the high solubility of the polymer.

Evidence for Chain-Growth in the Polycondensation Process. A key hurdle in our syntheses of polythiazoles is the need to employ "*reversed*" thiazole-monomers (i.e., 7- $Mg_{a/b}$) that are metalated at the sterically hindered 5-position, since "*regular*" metalation at the highly reactive 2-position leads to rapid decomposition of the monomer.²² As a consequence, initiation of the polymerization process is crucially different from the initiation of regular monomers (Scheme 2a). According to our current working hypothesis, initiation most likely proceeds through the sterically unfavorable formation of a head-to-headdyad (10) via Yamamoto-coupling or disproportionation of an intermediate aryl-nickel complex (9) generated from either a



Figure 4. WAXS refraction patterns of different polymer samples: (A1) pellet of C₉-PTz; (A2) pellet of C₁₃-PTz; (B1) PTzTIP as precipitated; (B2) PTzTIP after thermal treatment; (C1) pellet of PTzDIBO; (C2) PTzDIBO cooled from 150 °C. For details on the sample preparation, see the experimental section in the Supporting Information.

thiazolyl-Grignard species and Ni²⁺ or by oxidative addition (OA) of nonmetalated monomer onto Ni^{0.22} This is a significant difference to the polymerization of "*reversed*" thienyl-monomers, wherein the necessity to form an initial head-to-head-linkage reportedly hampers polymerization.^{6a,c,e} Polymerization of 7-Mg_b could be performed with either dichloro nickel precatalysts (Ni(L₂)Cl₂; L₂ = dppp, dppe, method A), or with L₂/Ni(cod)₂ as a Ni(0) source (method B). Both methods reliably furnish regioregular **PTzDIBO**, with either dppp or dppe as ligand. The polydispersities achieved with dppp were comparatively high (1.8–2.2 for $M_n \approx 100$ kDa), while dppe-based catalysts performed better under similar conditions (up to $M_n = 99.3$ kDa, PDI = 1.51, method B). Still, a correlation between the monomer/catalyst-ratio and the obtained molecular weights was



not observed, and the molecular weight generally far exceeded the value theoretically expected from the monomer/catalyst ratio (see e.g. Figure S10 in the Supporting Information). While these observations point toward the presence of a step-growth process, another reason may be that due to the complex initiation-steps and heterogeneous conditions (method A), initiation is sluggish and only a fraction of the introduced catalyst is actually involved in the polymerization. Furthermore, in method B formation of catalytically inactive Ni(dppp)₂/Ni(dppe)₂ may inadvertently lower the effective catalyst loading. In follow-up experiments these issues could be alleviated, however, by the use of aryl-nickel precatalysts that serve as external initiators (Scheme 2).

External initiation has been very successful in the synthesis of poly(thiophene)s,^{6c,40} and poly(dialkoxyphenylene)s,^{10a,b,d} leading to essentially defect-free polymers, lower PDIs, and better control over molecular weight and end-groups. Furthermore, tailored precatalysts allow the in-depth study of the polymerization mechanism,^{10a,b} and the introduction of functional end-groups.^{40b} In the present case, external initiation would allow to alleviate the steric hindrance in the first cross-coupling step, and would make it possible to employ a well-defined precatalyst in homogeneous solution.

Two aryl-nickel(dppe) complexes with o-methoxyphenyl (o-anisyl, C1) and *m*-xylyl substituents (C2) have been synthesized according to a modified procedure based on a previous report by McNeil and co-workers (Scheme 2, see Supporting Information for details).^{10d} The o-anisyl-complex C1 was chosen because the methoxy-substituent is sterically less demanding than an alkyl-group, while still providing some steric protection of the metal center.⁴¹ The *m*-xylyl-complex C2 is less sterically encumbered and initiation should therefore be faster, while the additional methyl groups improve solubility. C1 was found to be chemically robust and could be completely characterized by ¹H and ³¹P NMR, and mass spectrometry. The molecular structure of C1 could also be confirmed through single crystal X-ray diffraction (crystallographic data included in the Supporting Information). Catalyst C2 proved to be more sensitive to decomposition and was characterized via ¹H and ³¹P NMR.

Series of batch polymerizations were then carried out with both C1 and C2, according to method C with different monomerto-catalyst-ratios (Figures 5 and 6). Both catalysts showed a linear correlation between the molecular weight determined via GPC and the monomer/catalyst ratio (Figures 6A and 6B) and furnished



Figure 5. GPC chromatograms of batch-polymerization experiments (method C) and monomer/catalyst ratios: (A) catalyst C1; (B) catalyst C2.

material with low polydispersities (<1.4 up to M_n > 100 kDa), in accordance with a chain-growth process. **C2** performed particularly well with polydispersities below 1.2 up to molecular weights around 80 kDa. (monomer/catalyst-ratio =50/1). Only at very low catalyst loading (**C2**, monomer/catalyst ratio = 67/1 and 100/1) did the PDI begin to rise. The GPC-chromatograms typically showed a bimodal mass-distribution with shoulder bands and individual peaks that correspond to approximately twice the molecular weight of the main peak. The bimodal mass-distribution may be attributed either to high molecular weight species generated through chain—chain-coupling, as is commonly observed in polythiophene syntheses,^{6b,25a,42} or possibly to competing initiation pathways that lead do two different types of polymer. The reaction mixtures were quenched with methanol acidified with hydrochloric acid, which should prevent oxidative coupling



Figure 6. Plots of M_n and PDI vs monomer/catalyst to monomer ratio from batch polymerization experiments: (A) catalyst C1; (B) catalyst C2. Part A includes M_n -values both determined via GPC ($M_{n,GPC}$) and derived from NMR-data ($M_{n,NMR}$).

of the polymer chains during the work-up.^{6b} Chain-chaincoupling via disproportionation after consumption of the monomer may still have occurred. In order to further elucidate this matter different polymer-fractions from a batch polymerization with catalyst **C2** (catalyst/monomer ratio of 20:1; Figure SB) were separated via semipreparative GPC (see Figure S11 in the Supporting Information). The individual polymer-fractions exhibited number-average molecular weights of $M_n = 20.5$ kDa (PDI = 1.06) and $M_n = 42.8$ kDa (PDI = 1.05), respectively, in agreement with chain-chain-coupling after monomer consumption. Notably, the very low PDIs of the individual batches would indicate, that the polymerization process follows a well-controlled chain-growth-process.

Attempts to further elucidate the polymerization process by an analyses of the polymer-chain-end via mass spectrometry met with mixed results. Polymeric species of up to m/z = 12 kDa (batch: $M_{n,GPC} = 8.6$ kDa, catalyst C1, see Figure S12 in the Supporting Information) could be observed at low resolution via linear mode MALDI–ToF MS. The mass-spectra inadvertently showed different types of polymeric species that could not be assigned to specific end-groups due to the low resolution.

However, the incorporation of the precatalyst can be inferred from NMR data, in combination with a model compound synthesized via Negishi-coupling of two anisyl-moieties to monomer 1a (11, Scheme 2c). In ¹H NMR spectra of *o*-anisyl-capped polymers two characteristic singlets appear at 3.86 and 4.71 ppm, that are attributed to the methoxy group of the anisyl end-group, and the α -methylene group of the adjacent "head-to-head"-linked thiazole ring (Figure 7a-c). The ¹H NMR-spectrum of the model compound (Figure 7d) shows two signals for the chemically inequivalent methoxy groups of the head-to-tail- and headto-head-linked anisole-rings at 4.01 and 3.86 ppm, respectively, and a signal at 4.83 ppm assigned to the α -methylene group on the thiazole ring. Using the signal of the methoxy group as reference, the molecular weights of the respective polymer samples were calculated (Figure 6A, see also Figure S13 in the Supporting Information). The thus derived molecular weights for low molecular weight fractions were in good agreement with the ones determined via GPC, while at higher molecular weights (>30 kDa) NMR gave higher molecular weights than GPCanalyses. The good agreement of the ¹H NMR-properties of the model compound with the polymer samples clearly indicates incorporation of the anisyl-moiety into the polymer. At this point, we cannot confirm quantitative chain-end functionalization. Indeed, small amounts of head-to-head-defects are clearly



Figure 7. 1 H NMR spectra of batches of anisyl-capped PTzDIBO (a–c) and model compound 11 (d).

present in low molecular weight batches (Figure 7c) that might originate from initiation via the pathway outlined in Scheme 2a.

CONCLUSION

A synthetic access to *reversed* silyloxymethyl functionalized thiazole-monomers has been developed, which can be polymerized via Kumada-coupling polycondensation to furnish head-to-tail regioregular polythiazoles (*rr*-PTzs, PTzTIP, PTzDIBO). Owing to the incorporation of highly solubilizing diisobutyloctadecylsilyl-side-chains PTzDIBO is the first fully soluble polythiazole, and readily gave number-average molecular weights exceeding 100 kDa, corresponding to a degree of polymerization greater than 200. The presence of the bulky silyloxy side-chains affects the solid state structure of the polymers,

and leads to a lesser prevalence of π -stacking and a widened optical band gap, compared to 4-alkyl-substituted polythiazoles (C₉- and C₁₃-PTz). Still, cyclic voltammetry indicates largely similar electrochemical properties, in agreement with the isoelectronic nature of the conjugated π -systems. The great bulk of the side-chains required to render PTzDIBO soluble is likely detrimental for the performance of the polymer in organic electronic devices. Still, starting from the versatile intermediate **6** other side-chains may be introduced that furnish soluble PTzs better suited for device fabrication.

The investigation of the polymerization process through batch polymerizations with externally initiating aryl-nickel precatalyst indicated the presence of a chain-growth mechanism, as evidenced by very low polydispersities and a linear correlation between the obtained molecular weight and the monomer/catalyst ratio. Furthermore, the incorporation of the precatalyst-aryl moiety into the polymer chain could be proven and the molecular weights could thereby be independently derived via ¹H NMR. The good correlation between molecular weights derived from GPC and NMR corroborates both the proposed initiation pathway and the presence of a chain-growth mechanism. Given the very limited number of polyarenes that can be accessed via quasi-living polycondensation, the likely occurrence of chain-growth in the synthesis of head-to-tail regioregular polythiazoles constitutes a significant progress in the development of polymeric semiconductors.

ASSOCIATED CONTENT

Supporting Information

Experimental details, additional analytical data, and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*(F.P.) E-mail: frank.pammer@uni-ulm.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Markus Lamla and Bettina Stöckle for support with GPC measurements (THF), and Markus Wunderlin (Uni Ulm) and Agnes Fizia (TU Kaiserslautern) for assistance with mass spectrometry data collection. We also thank Harald Kelm and Dirk Schaffner from the TU Kaiserslautern and Ullrich Ziegler from Uni Ulm for support with NMR and CP-MAS NMR data collection. This work was supported by the Alexander von Humboldt foundation, the German Chemical Industry Fund (FCI) (Feodor-Lynen research fellowship and Liebig Scholarship to Frank Pammer), and the German Science Foundation (DFG).

REFERENCES

 (a) Inzelt, G. Conducting Polymers; Springer: Heidelberg, Germany, 2008. (b) Freund, M. S.; Deore, B. Self-Doped Conducting Polymers; Wiley: Chichester, U.K., 2007. (c) Skotheim, T. A.; Reynolds, J. R. Handbook of Conducting Polymers, 3rd ed.; CRC Press: Boca Raton, FL, 2007. (d) Hadziioannu, G.; Malliaras, G G. Semiconducting Polymers; Wiley-VCH: Weinheim, Germany, 2007. (e) Nalwa, H. S. Handbook of Conductive Organic Molecules and Polymers; Wiley-VCH: Weinheim, Germany, 1997. (f) Kuzmany, H.; Mehring, M.; Roth, S. Electronic Properties of Conjugated Polymers; Springer: Berlin and Heidelberg, Germany, 1987. (2) (a) Osaka, I.; McCullough, R. D. "Regioregular and regiosymmetric polythiophenes. In *Conjugated Polymer Synthesis;* Chujo, Y., Ed.; Wiley: New York, 2010, 59–90. (b) Osaka, I.; McCullough, R. D. Advanced functional regioregular polythiophenes. In *Design and Synthesis of Conjugated Polymers;* Leclerc, M.; Morin, J.-F., Eds.; Wiley-VCH: Weinheim, Germany, 2010; pp 91–145. (c) Perepichka, I. F.; Perepichka, D. F. *Handbook of Thiophene-based Materials: Applications in Organic Electronics and Photonics;* Wiley: Chichester, U.K., 2009. (d) Fichou, D. *Handbook of Oligo- and Polythiophenes;* Wiley-VCH: Weinheim, Germany, 1999.

(3) (a) Thomas, S. W., III; Joly, G. D.; Swager, T. M. Chem. Rev. 2007, 107, 1339–1386. (b) McQuade, D. T.; Pullen, A. E.; Swager, T. M. Chem. Rev. 2000, 100, 2537–2574.

(4) (a) Bryan, Z. J.; McNeil, A. J. *Macromlecules* **2013**, *46*, 8395–8405. (b) Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D. *Macromolecules* **2009**, *42*, 30–32. (c) Yokozawa, T.; Yokoyama, A. *Chem. Rev.* **2009**, *109*, 5595–5619. (d) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202–1214.

(5) (a) Grisorio, R.; Mastrorilli, P.; Suranna, G. P. *Polym. Chem.* 2014, DOI: 10.1039/C4PY00028E. (b) Yokozawa, T.; Suzuki, R.; Nojima, M.; Ohta, Y.; Yokoyama, A. *Macromol. Rapid Commun.* 2011, 32, 801–806. (c) Elmalem, E.; Kiriy, A.; Huck, W. T. S. *Macromolecules* 2011, 44, 9057–9061. (d) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. J. Am. Chem. Soc. 2007, 129, 7236–7237.

(6) (a) Tkachov, R.; Senkovskyy, V.; Komber, H.; Kiriy, A. *Macromolecules* **2011**, *44*, 2006–2015. (b) Thelakkat, M.; Lohwasser, R. H. *Macromolecules* **2011**, *44*, 3388–3397. (c) Senkovskyy, V.; Sommer, M.; Tkachov, R.; Komber, H.; Huck, W. T. S.; Kiriy, A. *Macromolecules* **2010**, *43*, 10157–10161. (d) Bronstein, H. A.; Luscombe, C. K. J. Am. Chem. Soc. **2009**, *131*, 12894–12895. (e) Boyd, S. D.; Jen, A. K.-Y.; Luscombe, C. K. *Macromolecules* **2009**, *42*, 9387–9389. (f) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324–4333.

(7) (a) Hollinger, J.; Jahnke, A. A.; Coombs, N.; Seferos, D. S. J. Am. Chem. Soc. 2010, 132, 8546–8547. (b) Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitus, G.; Bendikov, M. J. Am. Chem. Soc. 2008, 130, 6734–6736. (c) Heeney, M.; Zhang, W.; Crouch, D. J.; Chabinyc, M. L.; Gordeyev, S.; Hamilton, R.; Higgins, S. J.; McCulloch, I.; Skabara, P. J.; Sparrowe, D.; Tierney, S. Chem. Commun. 2007, 5061–5063.

(8) Huang, L.; Wu, S.; Qu, Y.; Geng, Y.; Wang, F. Macromolecules 2008, 41, 8944-8947.

(9) Yokoyama, A.; Kato, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2008**, *41*, 7271–7273.

(10) (a) Lee, S. R.; Bloom, J. W. G.; Wheeler, S. E.; McNeil, A. J. Dalton Trans. **2013**, 42, 4218–4222. (b) Lee, S. R.; Bryan, Z. J.; Wagner, A. M.; McNeil, A. J. Chem. Sci. **2012**, 3, 1562–1566. (c) Lanni, E. L.; Locke, J. R.; Gleave, C. M.; McNeil, A. J. Macromolecules **2011**, 44, 5136–5145. (d) Lanni, E. L.; McNeil, A. J. Macromolecules **2010**, 43, 8039–8044. (e) Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T. J. Am. Chem. Soc. **2006**, 128, 16012–16013.

(11) (a) Fukumoto, H.; Kimura, R.; Sasaki, S.; Kubota, K.; Yamamoto, T. J. Polym. Sci., Part B: Polym. Phys. 2005, 43, 215– 222. (b) Yokozawa, T.; Nanashima, Y.; Ohta, Y. Macro Lett. 2012, 1, 862–866. (c) Nanashima, Y.; Yokoyama, A.; Yokozawa, T. J. Polym. Sci. Part. A: Polym. Chem. 2012, 50, 1054–1061. (d) Nanashima, Y.; Yokoyama, A.; Yokozawa, T. Macromolecules 2012, 45, 2609–2613.

(12) (a) Yokozawa, T.; Nanashima, Y.; Ohta, Y. ACS Macro Lett. 2012, 1, 862–866. (b) Senkovskyy, V.; Tkachov, R.; Komber, H.; John, A.; Sommer, J.-U.; Kiriy, A. Macromolecules 2012, 45, 7770– 7777. (c) Senkovskyy, V.; Tkachov, R.; Komber, H.; John, A.; Sommer, M.; Heuken, M.; Voit, B.; Huck, W. T. S.; Kataev, V.; Peter, A.; Kiriy, A. J. Am. Chem. Soc. 2011, 133, 19966–19970.

(13) Bridges, C. R.; McCormick, T. M.; Gibson, G. L.; Hollinger, J.; Seferos, D. S. J. Am. Chem. Soc. **2013**, 135, 13212–13219.

(14) (a) Li, L.; Counts, K. E.; Kurosawa, S.; Teja, A. S.; Collard, D. M. Adv. Mater. 2004, 16, 180–183. (b) Li, L.; Collard, D. M. Macromolecules 2005, 38, 372–378. (c) Geng, Y.; Tajima, K.; Hashimoto, K. Macromol. Rapid Commun. 2011, 32, 1478–1483.

Macromolecules

(15) Wen, L.; Duck, B. C.; Dastoor, P. C.; Rasmussen, S. C. *Macromolecules* **2008**, *41*, 4576–4578.

(16) Bronstein, H.; Hurhangee, M.; Fregoso, E. C.; Beatrup, D.; Soon, Y. W.; Huang, Z.; Hadipour, A.; Tuladhar, P. S.; Rossbauer, S.; Sohn, E.; Shoaee, S.; Dimitrov, S. D.; Frost, J. M.; Ashraf, R. S.; Kirchartz, T.; Watkins, S. E.; Song, K.; Anthopoulos, T.; Nelson, J.; Rand, B. P.; Durrant, J. R.; McCulloch, I. *Chem. Mater.* **2013**, *25*, 4239–4249.

(17) (a) Mamada, M.; Nishida, J.; Kumaki, D.; Tokito, S.; Yamashita, Y. *Chem. Mater.* 2007, *19*, 5404–5409. (b) Ando, S.; Murakami, R.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* 2005, *127*, 14996–14997. (c) Akhtaruzzaman, M.; Kamata, N.; Nishida, J.; Ando, S.; Tada, H.; Tomurab, M.; Yamashita, Y. *Chem. Commun.* 2005, 3183–3185.

(18) Lin, Y.; Fan, H.; Li, Y.; Zhan, X. Adv. Mater. 2012, 24, 3087-3106. (19) Current examples: (a) Saeki, A.; Tsuji, M.; Yoshikawa, S.; Gopal, A.; Seki, S. J. Mater. Chem. A 2014, 17, 6075-6080. (b) Osaka, I.; Saito, M.; Koganezawa, T.; Takimiya, K. Adv. Mater. 2014, 26, 331-338. (c) Ren, G.; Schlenker, C. W.; Ahmed, E.; Subramaniyan, S.; Olthof, S.; Kahn, A.; Ginger, D. S.; Jenekhe, S. A. Adv. Funct. Mater. 2013, 23, 1238-1249. (d) Intemann, J. J.; Mike, J. F.; Cai, M.; Barnes, C. A.; Xiao, T.; Roggers, R. A.; Shinar, J.; Shinar, R.; Jeffries-El, Ma. J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 916-923. (e) Itaru, O.; Masahiko, S.; Hiroki, M.; Tomoyuki, K.; Kazuo, T. Adv. Mater. 2012, 24, 425-430. (f) Lu, W.; Kuwabara, J.; Kanbara, T. Polym. Chem. 2012, 3, 3217-3219. (g) Zhang, M.; Fan, H.; Guo, X.; Yang, Y.; Wang, S.; Zhang, Z.-G.; Zhang, J.; Zhan, X.; Li, Y. J. Polym. Sci., Part A: Polym. Chem. 2011, 49, 2746-2754. (h) Yamamoto, T.; Otsuka, S.-I.; Fukumoto, H.; Sakai, Y.; Aramaki, S.; Fukudo, T.; Emoto, A.; Ushijima, H. J. Polym. Sci., Part A: Polym. Chem. 2011, 49, 1508-1512. (i) Allard, N.; Beaupre, S.; Badrou, R.; Najari, A.; Tao, Y.; Leclerc, M. Macromolecules 2011, 44, 7184-7187. (j) Kudla, C. J.; Dolfen, D.; Schottler, K. J.; Koenen, J.-M.; Breusov, D.; Allard, S.; Scherf, U. Macromolecules 2010, 43, 7864-7867.

(20) (a) Mori, S.; Yamamoto, T.; Asakawa, N.; Yazawa, K.; Inoue, Y. Polym. J. 2008, 40, 475–478. (b) Mori, S.; Inoue, Y.; Yamamoto, T.; Asakawa, N. Phys. Rev. B 2005, 71, 054205–054205–11. (c) Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B.; Suganuma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. J. Am. Chem. Soc. 1998, 120, 2047–2058. (d) Yamamoto, T.; Suganuma, H.; Maruyama, T.; Inoue, T.; Muramatsu, Y.; Arai, M.; Komarudin, D.; Ooba, N.; Tomaru, S.; Sasaki, S.; Kubota, K. Chem. Mater. 1997, 9, 1217–1225. (e) Yamamoto, T.; Suganuma, H.; Maruyama, T.; Kubota, K. J. Chem. Soc., Chem. Commun. 1995, 1613–1614.

(21) (a) Politis, J. K.; Curtis, M. D.; González-Ronda, L.; Martin, D. C. Chem. Mater. 2000, 12, 2798–2804. (b) González-Ronda, L.; Martin, D. C.; Nanos, J. I.; Politis, J. K.; Curtis, M. D. Macromolecules 1999, 32, 4558–4565. (c) Politis, J. K.; Somoza, F. B., Jr.; Kampf, J. W.; Curtis, M. D.; González-Ronda, L.; Martin, D. C. Chem. Mater. 1999, 11, 2274–2284. (d) Politis, J. K.; Curtis, M. D.; He, Y.; Kanicki, J. Macromolecules 1999, 32, 2484–2489. (e) Curtis, M. D.; Cheng, H.; Johnson, J. A.; Nanos, J. I.; Kasim, R.; Elsenbaumer, R. L.; González-Ronda, L.; Martin, D. C. Chem. Mater. 1998, 10, 13–16. (f) Nanos, J. I.; Kampf, J. W.; Curtis, M. D. Chem. Mater. 1995, 7, 2232–2234. (22) Pammer, F.; Passlack, U. ACS Macro Lett. 2014, 3, 170–174.

(23) Molecular weights were determined via GPC in CHCl₃ at 35 °C relative to polystyrene standards. GPC-analyses of **PTzDIBO** with THF as eluent gave higher molecular weights than GPC in CHCl₃. (e.g., batches polymerized with Ni(dppe)Cl₂ gave $M_n = 122.6$ kDa, (PDI = 1.43) and 97.8 kDa, (PDI = 1.26), when analyzed in THF, while in CHCl₃ $M_n = 60.7$ (PDI = 1.50) and 44.5 kDa (PDI = 1.52) were measured for the same samples. For the soluble fraction of **PTzTIP** the maximum M_n observed in THF was 3.5 kDa (PDI = 1.44), as compared to 2.7 kDa (PDI = 1.30) measured in CHCl₃.

(24) Molecular weight determination of rod-like conjugated polymers vs coil-like polystyrene standards leads to overestimation of the apparent molecular weight (see literature included in ref 25 for details). The authors are aware of this systemic deviation. However, barring alternative means to determine the molecular weight, uncorrected molecular weights are reported. (25) (a) Wong, M.; Hollinger, J.; Kozycz, L. M.; McCormick, T. M.; Lu, Y.; Burns, D. C.; Seferos, D. S. *ACS Macro Lett.* **2012**, *1*, 1266– 1269. (b) Hiorns, R. C.; de Bettignies, R.; Leroy, J.; Bailly, S.; Firon, M.; Sentein, C.; Khoukh, A.; Preud'homme, H.; Dagron-Lartigau, C. *Adv. Funct. Mater.* **2006**, *16*, 2263–2273. (c) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777–5785.

(26) Strotman, N. A.; Chobanian, H. R.; He, J.; Guo, Y.; Dormer, P. G.; Jones, C. M.; Steves, J. E. J. Org. Chem. **2010**, 75, 1733–1739.

(27) Littke, A. F.; Fu, G. C. Angew. Chem., Int. Ed. 2002, 41, 4176–4211.

(28) **PTzDIBO**: 5.09 ppm at 25 °C and 5.11 ppm at 50 °C in CDCl₃; 5.27 ppm at 100 °C in ODCB-d₄. **PTzTIP**: 5.28 ppm at 150 °C in ODCB-d₄. **PBTzTIP**: 4.88 ppm at 25° in CDCl₃; 5.00 ppm at 100 °C in ODCB-d₄.

(29) Chen, T.; Wu, X.; Rieke, R. D. J. Am. Chem. Soc. 1995, 117, 233-244.

(30) Pammer, F.; Guo, F.; Lalancette, R. A.; Jäkle, F. *Macromolecules* **2012**, *45*, 6333–6343.

(31) Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B.-L.; Suganuma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. J. Am. Chem. Soc. **1998**, *120*, 2047–2058.

(32) (a) Cook, S.; Furube, A.; Katoh, R. *Energy Environ. Sci.* **2008**, *1*, 294–299. (b) Li, Y.; Vamvounis, G.; Holdcroft, S. *Macromolecules* **2002**, 35, 6900–6906.

(33) (a) Panzer, F.; Bässler, H.; Lohwasser, R.; Thelakkat, M.; Köhler, A. J. Phys. Chem. Lett. **2014**, 5 (15), 2742–2747. (b) Adachi, T.; Brazard, J.; Ono, R. J.; Hanson, B.; Traub, M. C.; Wu, Z.-Q.; Li, Z.; Bolinger, J. C.; Ganesan, V.; Bielawski, C. W.; Vanden Bout, D. A.; Barbara, P. F. J. Phys. Chem. Lett. **2011**, 2, 1400–1404.

(34) Zhou, G.; Qian, G.; Ma, L.; Cheng, Y.; Xie, Z.; Wang, L.; Jing, X.; Wang, F. *Macromolecules* **2005**, *38*, 5416–5424.

(35) Nehls, B. S.; Füldner, S.; Preis, E.; Farrell, T.; Scherf, U. *Macromolecules* **2005**, *38*, 687–694.

(36) (a) Huang, H.; Zhou, N.; Ortiz, R. P.; Chen, Z.; Loser, S.; Zhang, S.; Guo, X.; Casado, J.; López Navarrete, J. T.; Yu, X.; Facchetti, A.; Marks, T. J. Adv. Funct. Mater. 2014, 3016–3028.
(b) Guo, X.; Quinn, J.; Chen, Z.; Usta, H.; Zheng, Y.; Xia, Y.; Hennek, J. W.; Ortiz, R. P.; Marks, T. J.; Facchetti, A. J. Am. Chem. Soc. 2013, 135, 1986–1996. (c) Guo, X.; Ortiz, R. P.; Zheng, Y.; Kim, M.-G.; Zhang, S.; Hu, Y.; Lu, G.; Facchetti, A.; Marks, T. J. J. Am. Chem. Soc. 2011, 133, 13685–13697. (d) Guo, X.; Kim, F. S.; Jenekhe, S. A.; Watson, M. D. J. Am. Chem. Soc. 2009, 131, 7206–7207. (e) Roncali, J.; Blanchard, P.; Frere, P. J. Mater. Chem. 2005, 15, 1589–1610.

(37) Zoombelt, A. P.; Leenen, M. A. M.; Fonrodona, M.; Wienk, M. M.; Janssen, R. A. J. *Thin Solid Films* **2008**, *516*, 7176–7180.

(38) Fontana, L.; Vinh, D. Q.; Santoro, M.; Scandolo, S.; Gorelli, F. A.; Bini, R.; Hanfland, M. *Phys. Rev. B* **2007**, *75*, 174112 (1–11).

(39) (a) Thompson, B. C.; Kim, Y.-G.; McCarley, T. D.; Reynolds, J. R. J. Am. Chem. Soc. **2006**, 128, 12714–12725. (b) Hansen, W. N.; Hansen, G. J. Phys. Rev. A: At., Mol., Opt. Phys. **1987**, 36, 1396–1402. (c) Pavlishchuk, V. V.; Addison, A. W. Inorg. Chim. Acta **2000**, 298, 97–102.

(40) (a) Chavez, C. A.; Choi, J.; Nesterov, E. E. Macromolecules 2014,
47, 506–516. (b) Smeets, A.; Willot, P.; De Winter, J.; Gerbaux, P.;
Verbiest, T.; Koeckelberghs, G. Macromolecules 2011, 44, 6017–6025.
(c) Komber, H.; Senkovskyy, V.; Tkachov, R.; Johnson, K.; Kiriy, A.;
Huck, W. T. S.; Sommer, M. Macromolecules 2011, 44, 9164–9172.
(d) Tkachov, R.; Senkovskyy, V.; Komber, H.; Sommer, J.-U.; Kiriy, A.
J. Am. Chem. Soc. 2010, 132, 7803–7810. (e) Doubina, N.; Stoddard,
M.; Bronstein, H. A.; Jen, A. K.-Y.; Luscombe, C. K. Macromol. Chem.
Phys. 2009, 210, 1966–1972. (f) Senkovskyy, V.; Khanduyeva, N.;
Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriy, A. J. Am.
Chem. Soc. 2007, 129, 6626–6632.

(41) Ortho-substituted nickel-aryl complexes are generally found to be more stable than unsubstituted derivatives. See also (a) Hidai, M.; Kashiwagi, T.; Ikeuchi, T.; Uchida, Y. J. Organomet. Chem. 1971, 30, 279–282. (b) Chatt, J.; Shaw, B. L. J. Chem. Soc. 1960, 1718–1729. (42) Achord, B. C.; Rawlins, J. W. Macromolecules 2009, 42, 8634–8639.