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Use of Highly Reactive Zinc Leads to a New, Facile Synthesis for Polyarylenes

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The chemical synthesis of polyarylenes, such as poly(*p*-phenylene) (PPP) and poly(thiophene-2,5-diyl) (PTh), by catalyzed dedihalogenation of 1,4-dihaloaromatic and 2,5-dihaloaromatic is an important method in the synthesis of conjugated conducting polymers.¹ Among these, the Ni-catalyzed polymerization of Grignard reagents² and the one-pot dedihalogenational polymerization of dihaloarylenes by a stoichiometric amount of a Ni(II) complex and a base in combination with a large excess of commercial zinc dust³ have been extensively investigated. Recent reports have shown a HMPA- or THF-promoted polymerization of dibromobenzene via a monolithiobenzene intermediate afforded a soluble poly(*p*-phenylene),^{1b,4} and a polymerization of dihaloarylene by a stoichiometric amount of a Ni(0) complex and a base has been developed.⁵ We now report a facile and effective Pd-catalyzed polymerization of monozinc aryls, such as iodo-4-(iodozincio)benzene (3) and 2-bromo-5-(bromozincio)thiophene (4), which were generated by the reaction of highly reactive zinc (Zn*)⁶ and a dihaloarylene, to quantitatively yield polyarylenes.^{7,8}

The monoorganozinc aryls were readily generated by reaction of a 1.0:1.1 ratio of dihaloarylene (1 and 2) and highly reactive zinc (Zn*). Surprisingly, the reaction was totally chemoselective (>99%), as no bis(halozinc) arylene was found⁹ (Scheme I). The resultant monozinc intermediates (3 and 4) were polymerized upon the addition of a catalytic amount of Pd(PPh₃)₄ (≤0.2 mol %) and gave a quantitative yield (>98%) of polyarylene¹⁰ [PPP (5) and PTh (6); Scheme I]. The polymerization is based on Negishi's coupling reaction involving an organozinc reagent and a Pd catalyst.¹¹

In contrast, previous reports³ have examined the polymerization of dihaloarylene using a stoichiometric amount of Ni(II) complexes and base in combination with a large excess of commercial zinc dust. An identical result can be obtained using a stoichiometric amount of Ni(0) complexes, "catalyst", and a stoichiometric amount of base.⁵ It appears that the role of zinc dust is that of a reducing agent for Ni(II) to Ni(0).^{5b,12} In our synthesis, the highly reactive Zn*⁶ undergoes oxidative addition regioselectively to the dihaloarylene.

We have expanded this methodology to include 3-substituted dibromothiophene derivatives such as 3-decyl,¹³ -hexyl,⁸ -methyl, -phenyl, and -cyclopentyl¹⁴ utilizing Pd(PPh₃)₄ as the catalyst which results in a series of poly(3-substituted thiophenes) including a new P3AT: poly(3-cyclopentylthiophene) (Scheme II and Table I).

Upon workup,³ polymer 5 (PPP) yielded a light yellow powder, polymer 6 (PTh) a dark-red powder, and polymer 10a (P3MT) a red powder. All three polymers are insoluble

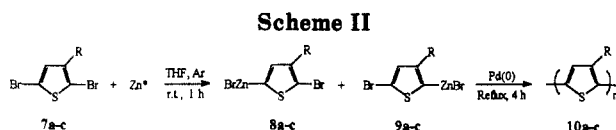
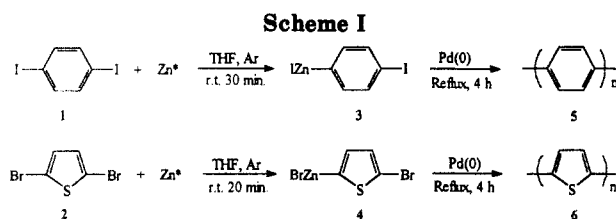


Table I. Poly(3-substituted thiophenes)*

reactant 7: -R	regioselectivity ^b (%)		polym yield ^c (%) of 10
	8	9	
a -CH ₃	80	20	98
b cyclopentyl	71	29	96
c -Ph	66	34	98

* Reactant ratio, 7:Zn* = 1.0:1.1. Catalyst amount: Pd(PPh₃)₄ 0.2 mol % of 7. ^b The yield of two regioisomers was >98% by GC analysis. The regioselectivity was identified by ¹H NMR analysis of the crude reaction mixture after quenching with a saturated NH₄Cl solution. ^c Based on carbon recovered.³

solids. Polymer 10b (poly(3-cyclopentylthiophene)) was an orange powder while polymer 10c (poly(3-phenylthiophene)) gave a dark-brown powder. Both 10b and 10c were soluble in CHCl₃, THF, or other polar organic solvents.

Elemental analysis values of all five polymers in Table I (5, 6, and 10a-c) compare well with calculated values. FTIR analysis of polymer 5 (PPP) yields a strong para C-H out-of-plane absorption band at 804 cm⁻¹ for *p*-phenylene.^{2a} Polymer 6 (PTh) has a strong absorbance at 792 cm⁻¹ for an aromatic C-H out-of-plane band for a 2,5-disubstituted thiophene, a weak C-H stretching absorbance at 3060 cm⁻¹, and thiophene ring stretching modes at 1441, 1456, and 1490 cm⁻¹.^{2c,15} Polymer 10a (P3MT) has a C-H out-of-plane vibration band for 3-methyl-2,5-thienylene at 817 cm⁻¹ and thienylene ring stretching modes at 1439, 1458, and 1506 cm⁻¹.¹⁵ Polymer 10b (P3CpT) has a strong absorbance at 800 cm⁻¹ for an aromatic C-H out-of-plane vibration for 3-cyclopentyl-2,5-thienylene and a weak band at 3052 cm⁻¹ for C-H stretching. Also, thienylene ring stretching modes were found at 1437, 1456, and 1506 cm⁻¹ and at 2864 and 2974 cm⁻¹ for aliphatic C-H stretching modes of the cyclopentyl group. Polymer 10c (P3PhT) has a thiophene ring C-H out-of-plane bend for 3-phenyl-2,5-thienylene found at 839 cm⁻¹, at 3057 cm⁻¹ for C-H stretching, thiophene ring stretching modes at 1444, 1481, and 1495 cm⁻¹, at 697 and 758 cm⁻¹ for ring banding,^{3b} and at 3008 and 3027 cm⁻¹ for C-H stretching of a monosubstituted benzene group.

Solid-state ¹³C NMR analysis of 10a (P3MT) shows there are four carbons around 132 ppm for four thiophene ring carbons and one carbon at 15 ppm for a methyl group based on carbon integration. ¹H NMR analysis of 10b (P3CpT) gave a spectrum which contains 1 H at 7.03 ppm for the thiophene ring proton, 1 H at 3.44 ppm for a tertiary

proton (pentant), and 8 H's at 1.25–2.04 ppm for the secondary protons of the cyclopentyl group. For polymer 10c (P3PhT), there are 5 H's at 7.2–7.6 ppm for the phenyl protons and 1 H at 7.13 ppm for the thiophene ring proton.

The UV-vis spectrum of 10b shows a maximum absorption at $\lambda = 413$ nm (CHCl_3) for a $\pi\text{--}\pi^*$ electronic transition which depends on the conjugated length of the polymer. Another absorption maximum was found at $\lambda = 263$ nm for a $\pi\text{--}\pi^*$ transition, which is not dependent upon the conjugated length.¹⁶ For 10c (P3PhT), the conjugated $\pi\text{--}\pi^*$ transition also has an absorption wavelength of 410 nm, but the non-conjugated $\pi\text{--}\pi^*$ transition of the thiophene ring was covered by a more intense absorption at $\lambda = 254$ nm, which was exactly the same as for an isolated benzene $\pi\text{--}\pi^*$ transition wavelength.¹⁷ This implies the benzene ring is not conjugated with a thiophene ring and suggests that the two planes are essentially nonplanar by a torsion angle $>40^\circ$ due to a steric hindrance.¹⁸ The calculated molecular weight of polymer 10c (P3PhT) was 4912 based on the terminal Br group content,^{2c} meanwhile GPC (gel permeation chromatography, relative to polystyrene standard, THF as eluant) yielded a weight-average molecular weight $M_w = 3900$ and a number-average molecular weight $M_n = 1969$ with a polydispersity index of 1.79.

In summary, the methodology reported within this paper provides several advantages over existing methods including the use of highly reactive zinc (1.1 equiv to 1.0 equiv of dihalide) in conjunction with a very small amount of catalyst, the quantitative chemoselectivity of Zn^* for dihaloarenes, and the mild reaction conditions and the higher yields of polymers make this method facile and effective for the preparation of polyphenylenes and polythiophenes.

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Supplementary Material Available: Figures of ^{13}C and ^1H NMR spectra of 10a–c, starting materials 2,5-dibromo-3-cyclopentylthiophene and -3-phenylthiophene, and regiorandom and regioregular poly(3-hexylthiophene), UV-vis spectra of 10b–c, and elemental analyses of 5, 6, and 10a–c (13 pages). Ordering information is given on any current masthead page.

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- (7) A patent application covering the technology described herein has been filed by the authors of this paper.
- (8) This method has recently been used in a totally regiocontrolled synthesis of poly(3-hexylthiophenes). See: Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* 1992, 114, 10087.
- (9) The yield of organozinc intermediates was based on GC analysis of a quenched reaction mixture with saturated NH_4Cl solution.
- (10) Typical procedure for the formation of highly reactive zinc (Zn^*): ZnCl_2 (4.10 mmol) in freshly distilled THF (15 mL) was transferred dropwise via cannula to a flask containing lithium (8.00 mmol), a catalytic amount of naphthalene (0.40 mmol), and THF (15 mL), until all the lithium was consumed (about 2 h) at room temperature. Typical synthesis procedure for polyarylenes, for example, 10a (P3MT): 2,5-dibromo-3-methylthiophene (4.0 mmol, in 15 mL of THF) was added via cannula to the freshly prepared highly reactive Zn^* (4.4 mmol) in THF (30 mL). The mixture was stirred for 1 h at room temperature under argon (in a dual-manifold system). At this time, $\text{Pd}(\text{PPh}_3)_4$ (0.008 mmol) in THF (10 mL) was added to the reaction mixture via cannula. After refluxing for 4 h, a deep-red precipitate appeared. The resultant mixture was cooled to room temperature and poured into a solution of MeOH (100 mL) and 2 N HCl (50 mL). The polymer was then filtered, washed with several portions of MeOH, 2 N HCl, and MeOH, and reprecipitated from CHCl_3 upon addition of MeOH. The polymer was dried at 80–90 $^\circ\text{C}$ for 24 h under vacuum to give the final product. This gave poly(3-methylthiophene) as a red powder with a yield greater than 98%, based on carbon recovered. Other polymers were synthesized in an analogous manner.
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