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Organolithium-Activated Nickel (OLAN) Catalysis: A New Synthetic Route for Polyarylates

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Conjugated polymers have attracted much attention because of their potential optoelectronic and biological applications, such as light-emitting diodes, photovoltaic devices, field-effect transistors, nonlinear optics, and chemical and biological sensors.[1] Among the conjugated polymers, polyfluorenes are being considered by many research and industrial groups as a very promising blue light-emitting material due to their high photoluminescence quantum yield, high thermal and chemical stability, ease of emission color tuning, facile modification at the 9-position of the fluorene ring without affecting main-chain conjugation, and patternability.[2,3]

Conjugated polymers containing aryl groups have been widely synthesized using various transition-metal-catalyzed or mediated step-growth polymerization techniques (Suzuki,[4,5] Yamamoto,[6,7] Haghihara/Sonogashira,[8] and Kumada/GRIM[9−11]). Because of the synthetic requirement of specific coupling functionalities within the monomer units (boronic acid for Suzuki, terminal alkynes for Sonogashira, and activated halogens for Kumada/GRIM), the synthesis of these materials is often a challenge for chemists. Yamamoto-type polycondensations of dihalogenated fluorenes have been widely used in the literature to produce a variety of polyfluorene homo- and copolymers.[12−22] For the polymerization of dibromofluorenes, polymers with M_n as high as 200 000 g/mol have been reported. The microwave-assisted coupling procedure has been reported to increase the yield of the polymer and decrease the polymerization time significantly.[23] Unfortunately, the Yamamoto polycondensation reaction involves the use of an equimolar amount of Ni(cyclooctadiene)$_2$ with respect to the monomer. So while highly useful, it is not a very cost-effective or convenient technique for polymerization since it requires large amounts of an expensive reagent and extended reaction times at elevated temperatures.

Coupling reactions that employ catalytic amounts of Ni have been developed and many require the addition of either magnesium or zinc reagents to facilitate efficient coupling and regeneration of active Ni(0) catalytic species. For example, Kumada coupling reactions use Mg for the formation of the active alkyl/aryl-magnesium bromide species (Grignard formation) which is generally a substrate and solvent-specific reaction (working optimally in tetrahydrofuran or ether).[24−28] Nickel reactions facilitated by added zinc have also been utilized in a similar fashion in organic synthesis[29−31] as well as in efficient condensation polymerizations.[32−34] These reactions are not always well controlled and require prolonged heating at high temperatures, and the products have high levels of metal impurities that can be difficult and costly to remove. This trace metal contamination is especially problematic if the end use is in pharmaceutical or microelectronic applications where safety, performance, and reliability require stringent control of purity. Coupling reactions involving activated dihalogenated thiophene molecules catalyzed by nickel(II) complexes have also been demonstrated in the presence of reactive zinc (Rieke zinc)[35] or an alkyl-magnesium reagent (GRIM/McCullough method)[9] to form regioregular polythiophenes.

We now report a novel synthetic route for the one-step, one-pot synthesis of polyarylene polymers. Organolithium-activated nickel catalysis, or OLAN, facilitates the polycondensation of 9,9-dihexyl-2,7-dibromofluorene by using organolithium as a reagent, a catalytic amount of 1,3-diphenylphosphinopropanenickel(II) chloride, (Ni(dppp)Cl$_2$), and bipyridine (bpy) at 0 °C, yielding poly(9,9-dihexyl-2,7-dibromofluorene) (Figure 1). In a typical OLAN polymerization, the monomer 9,9-dihexyl-2,7-dibromofluorene (250 mg, 0.51 mmol), Ni(dppp)Cl$_2$ (4 mg, 7.38 μmol), and bipyridine (2.8 mg, 17.93 μmol) were added to a flask containing anhydrous THF (2 mL). The flask was sealed under nitrogen, the reaction was cooled to 0 °C under an ice bath with stirring, and 0.3 mL of *t*-BuLi solution (0.48 mmol, 1.6 M solution in pentane) was added dropwise with a syringe. The mixture was allowed to gradually warm to room temperature and allowed to stir overnight. The polymer was diluted with THF and precipitated by adding the solution dropwise in dilute HCl (0.1 N), filtered, washed with acetone to remove unreacted monomer and oligomers, and dried to obtain polyfluorene (90 mg, 53%, $M_n = 33\,393$, PDI = 2.07) as an off-white powder. The ^{1}H and ^{13}C NMR spectra of the polymer were identical to previously synthesized poly(9,9-dihexylfluorene) using Yamamoto polycondensation techniques.

The efficient homocoupling of a variety of aryl bromide compounds including phenyl, pyrenyl, naphthyl, and fluorenyl bromide using the OLAN catalyst system has recently been reported.[36] The exact nature of the catalytic cycle (see Supporting Information Scheme 1) is proposed to involve the transmetalation of the aryllithium intermediate with a Ni(II) species. This is followed by a second transmetalation of the Ar−Ni(II)−X species to form an Ar−Ni(II)−Ar, which undergoes reductive elimination to form the Ar−Ar coupled product and active Ni(0).

The active Ni(0) species can subsequently undergo oxidative addition to another Ar−Br molecule. The reaction cycle affords the usage of catalytic amounts of nickel and the reaction yields were not sensitive to the amount of Ni(dppp)Cl$_2$, although the use of 0.5 equiv of *t*-BuLi to Ar−Br was important. Either an excess or insufficient amount of *t*-BuLi led to lower yields since the in situ generated Ni(0) species generated required sufficient amounts of aryl bromide for complete reactions. While we cannot exclude the possibility of some reduction of Ni(II) to Ni(0) by *t*-BuLi, this is not a major factor in the coupling reaction. The sequence of addition of the reagents is critical; if *t*-BuLi is first added to a solution containing Ni(II) followed by addition of Ar−Br, no product formation is observed. This exact nature of the coupling mechanism is currently under study.

It was observed that *n*-butyl-, *sec*-butyl-, and *tert*-butyllithium reagents could all be used to activate the polymerizations. Table 1

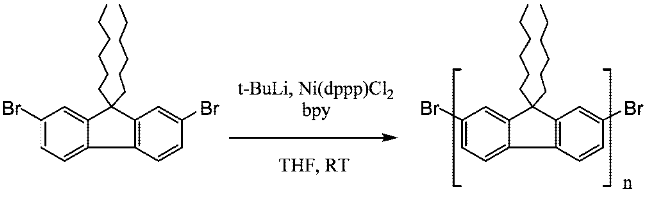

Figure 1. A one-step, one-pot synthesis of polyfluorene polymers via polycondensation of dihalogenated monomers.

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Table 1. Synthesis of Poly(9,9-dihexylfluorene) Using Different Alkyllithium Reagents and Varying Amounts of Catalyst and Bipyridine (bpy)[a]

	monomer **1**				R−Li		yield[b]			
R-Li	(mg)	(mmol)	$Ni(dppp)Cl_2$ (mg)	Bpy (mg)	(mL)	(mmol)	(mg)	(%)	M_n[c]	PDI[c]
n-BuLi	250	0.51	1.2	2.0	0.32	0.51	100	59	32 660	1.92
n-BuLi	250	0.51	1.2	2.0	0.78	1.25	100		<1 800	
sec-BuLi	250	0.51	4.0	2.8	0.36	0.51	95	56	22 830	1.97
t-BuLi	250	0.51	2.0	4.0	0.30	0.45	50	30	24 840	2.30
t-BuLi	250	0.51	1.0	1.8	0.28	0.42	135	80	23 650	2.91
t-BuLi	250	0.51	2.0	1.4	0.50	0.75	128	76	16 880	2.16

[a] $Ni(dppp)Cl_2$ = 4 mg, bpy = 2.8 mg, THF = 2 mL. *t*-BuLi solution (1.5 M in pentane) was added at 0 °C followed by stirring at room temperature for 24 h. [b] Yields are based upon weight of dried polymer isolated after precipitation in water followed by water and acetone washes. [c] M_n and PDI were obtained by GPC in THF using polystyrene standards.

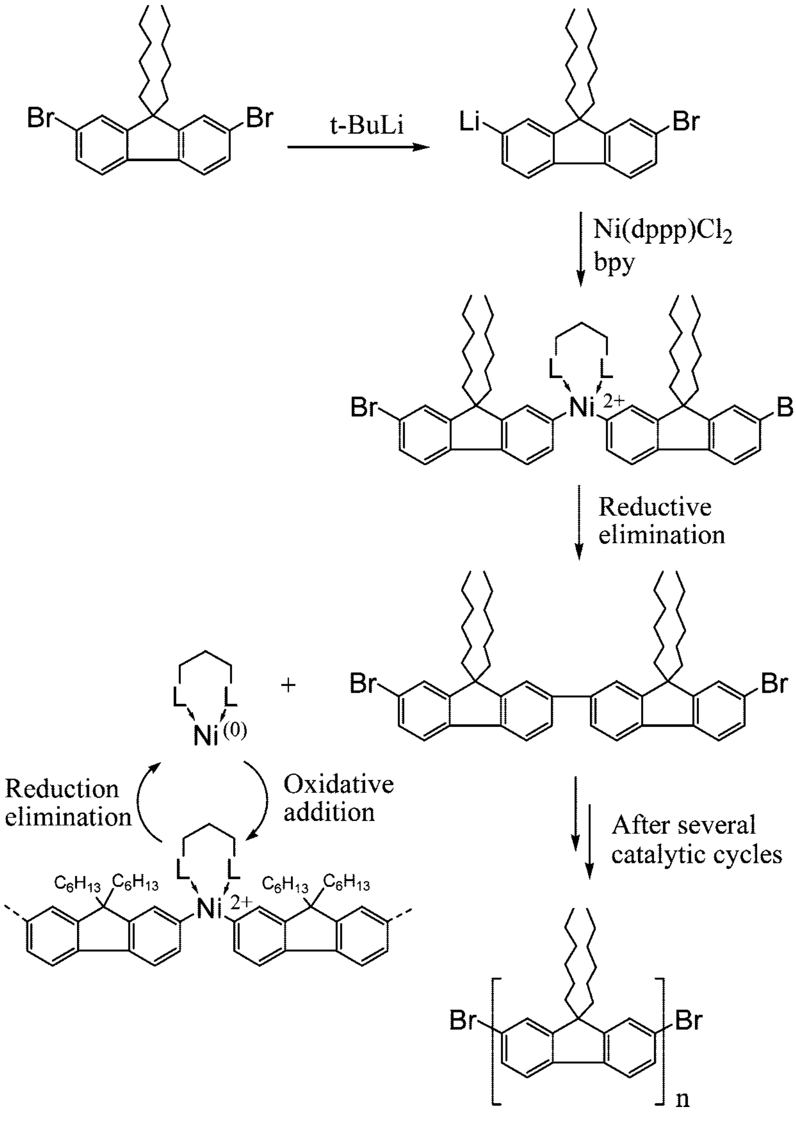

Figure 2. Proposed mechanism of nickel-catalyzed polycondensation reaction, including the catalytic cycle of nickel.

displays the data obtained from synthesis of poly(9,9-dihexylfluorene) using different alkyllithium reagents and amounts of catalyst and reagents. While there may be a slight tendency of primary alkyllithium reagents to undergo alkyl cross-coupling in place of lithiation, tertiary alkyllithiums do not give cross-coupled products in appreciable yields.[37] The alkyllithium reagents were added to the reaction mixture dropwise at 0 °C to reduce their interactions with THF. The relative amounts of Ni(II) and bpy were varied as shown in the entries of Table 1, with no trend observed in the polymerization data corresponding to the amount Ni catalyst used. The ligand bpy was added as it is known that the addition of bidentate ligands such as dppp and bpy can facilitate similar Ni-catalyzed coupling reactions.[38−40] The polymerization does not proceed in the absence of ligand (i.e., $NiCl_2$ catalyst alone). Other than ensuring the presence of bidentate ligand, no systematic study of the relative effect of ligand was performed.

In most of the polymerizations, the solution gelled at reaction times of 12−24 h due to the formation of high-MW polyfluorene which has reduced solubility in THF. The polymer from solution was diluted with additional THF and precipitated in water/dilute HCl (0.1 N) and washed several times with acetone. The observed

Table 2. Polymerization Data as a Function of the Amount of *t*-BuLi Used[a]

monomer **1**		*t*-BuLi		yield[b]			
(mg)	(mmol)	(mL)	(mmol)	(mg)	(%)	M_n[c]	PDI[c]
250	0.51	0.30	0.45	90	53	33 390	2.07
250	0.51	0.50	0.75	105	62	22 870	2.07
250	0.51	0.68	1.02	187	99	6 100	2.88
250	0.51	0.86	1.29	52	31	3 510	3.35

[a] Ni(dppp)Cl_2 = 4 mg, bpy = 2.8 mg, THF = 2 mL. *t*-BuLi solution (1.5 M in pentane) was added at 0 °C followed by stirring at room temperature for 24 h. [b] Yields are based upon weight of dried polymer isolated after precipitation in water followed by water and acetone washes. [c] M_n and PDI were obtained by GPC in THF using polystyrene standards.

molecular weight distributions were consistent with the proposed step-growth polymerization mechanism in Figure 1.

As predicted by the proposed mechanism, the ratio of alkyllithium reagent to monomer had a direct effect on molecular weight (Table 2). As the amount of *t*-BuLi was increased from 0.88 to 2.53 equiv with respect to monomer, the MW of the polymers decreased from 33 400 to 3500 g/mol. This is due to the need for precisely 0.5 equiv of *t*-BuLi for each equivalent of aromatic bromide. An excess of alkyllithium depletes the amount of bromofluorene groups needed for oxidative addition of Ni(0). Thus, an optimum ratio of the anion and bromofluorene is needed for a good turnover frequency of the catalytic system, resulting in the formation of high-MW polymer. When the polymerization was attempted with a similar 2.5 molar excess of *n*-BuLi, low molecular weight oligomers were also isolated as products. In reactions where the optimum ratio of 2:1 (monomer to *t*-BuLi), no evolution of isobutene was observed, and any reaction of *t*-BuLi with *t*-BuBr is thought to be minimal.

Since microwave-assisted Yamamoto polymerization of the dibromofluorene monomer (**1**) has been reported to increase the yield of the polymer and decrease the polymerization time significantly,[23] we decided to apply this technique to the OLAN system. After the addition of *t*-BuLi to the monomer/catalyst system at 0 °C, the reaction was allowed to gradually warm to room temperature (~15 min) and heated at 140 °C for 30 min. After cooling, the polymer was diluted with THF, filtered, and precipitated yielding polymer with MW as high as 25 000 g/mol (see Supporting Information). These results indicate that the yields and MW of the polymers obtained by microwave assisted synthesis in ~30 min were comparable to or better than those obtained via room temperature synthesis which were run for 24 h.

We present OLAN catalyzed polymerization as an important new technique for the synthesis of semiconducting polymers. The ease and effectiveness of this one-pot synthetic technique demonstrates the first example of the use of alkyllithium reagents with a nickel catalyst system to synthesize polymers. Although alkyllithiums are normally considered highly reactive in THF, they were effectively used to give polyfluorene of high molecular weight. We have demonstrated that OLAN works well for monomers that do not contain functionality sensitive to alkyllithium reagents, and we are currently exploring the mechanism, utility, and limitations of this reaction and how widely applicable this method may be toward the synthesis of other classes of semiconducting polymers.

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Supporting Information Available: Detailed experimental procedure, gel permeation chromatography (GPC) data, microwave polymerization data, and the proposed OLAN catalytic cycle. This material is available free of charge via the Internet at http://pubs.acs.org.

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