Grignard Metathesis Method (GRIM): Toward a Universal Method for the Synthesis of Conjugated Polymers

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Introduction. Plastic electronics, initiated by the discovery of conductivity in doped polyacetylene,[1] is an emerging field within chemistry that has immediate commercial applications ranging from organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), and solar cells.[2] Regardless of the usage, the synthesis of high-quality, high-purity materials is requisite for successful device design and implementation. A good example of the conjugated polymers found in these architectures is regioregular poly(3-hexylthiophene), which is usually synthesized by transition-metal-mediated cross-coupling,[3−5] including the Grignard metathesis (GRIM) method. In GRIM, Ni(II) complexes are used to polymerize functionalized Grignard monomers at room temperature, an advantage over previous procedures that once required cryogenic conditions. To expand GRIM applicability, we explored the use of "turbo-Grignard" reagents (LiCl plus a Grignard reagent)[6] in the synthesis of a variety of aryl and heteroaryl conjugated polymers. We found increased reactivity (lower reaction times and temperatures) for various monomers including 9,9-dioctyl-2,7-dibromofluorene, 2,5-dibromo-*N*-dodecylpyrrole, and 2,7-dibromo-*N*-octylcarbazole. This Communication outlines the synthesis of the turbo-Grignard reagents, their polymerization conditions, and characterization.

Applying the GRIM method to the synthesis of other aryl- and heteroaryl-based conjugated polymers has been a major research goal. In general, the syntheses of these other polymers are performed through metal-catalyzed polycondensation reactions based on Yamamoto, Suzuki, or Stille coupling reactions. Polymerization using any one of these methods usually requires 2−3 days and high temperatures (>100 °C). However, employing the GRIM method can shorten polymerization times and lower reaction temperatures, facilitating the preparation of aryl and heteroaryl conjugating polymers. Yokozawa et al. have recently reported that they were able to polymerize 1,4-dibromo-2,5-dihexyloxybenzene by the GRIM method through the addition of LiCl during the magnesium−halogen exchange reaction, giving well-defined poly(*p*-phenylene).[6−8] Here we present a more universal polymerization "universal GRIM", which can be used with other aryl and heteroaryl monomers. This method enables lower reaction temperatures and shorter polymerization times. Using one standard mode of polymerization also paves the way toward the production of block or random copolymers. These may have very different properties from or perform better in electronic applications compared to homopolymers.

Results and Discussion. Our initial attention was directed toward polyfluorenes, which are an important class of electroactive and photoactive materials.[9−11] They are highly studied because of their exceptional electro-optical properties and their exceptional performance in light-emitting diodes. They are capable of emitting colors spanning the entire visible range with high efficiency and low operating voltage. Substitution of two alkyl chains at the 9 and 9′ positions has led to a highly processable polymer derivative, poly(9,9′-dialkylfluorene) (PF), which also has a well-defined structure due to regioregularity. The dibrominated monomer is readily available commercially and is used for most of this study.

PF is usually synthesized through different polycondensation reactions with metal catalysts, among them Suzuki, Yamamoto, and Stille coupling reactions. Polymerization using any one of these methods usually requires 2−3 days and high temperatures (>100 °C) to yield high molecular weight polymers with broad polydispersities. However, employing the universal GRIM method enabled both shorter polymerization times and lower reaction temperatures.

PFs are less reactive in the magnesium halogen exchange process, preventing the use of normal Grignard metathesis (GRIM) as polymerization method. However, it has been previously reported by Knochel and co-workers that the addition of LiCl to isopropylmagnesium chloride leads to enhanced reactivity.[12] The addition of lithium chloride to a Grignard reagent turns it into what is called a "turbo-Grignard" and breaks the polymeric aggregates formed in solution to produce a very reactive complex, [i-PrMgCl$_2^-$Li$^+$]. The magnesiate character of complex 2 [i-PrMgCl$_2^-$Li$^+$] may be responsible for the enhanced reactivity of this reagent. In addition, the LiCl additive can be replaced with other lithium, magnesium, or zinc salts.

Magnesium halogen exchange can also be performed with magnesium ate complexes such as R$_3$MgLi, where R = *n*-Bu, *t*-Bu, or *i*-Pr.[13−15] The first magnesium halogen exchange reactions via organomagnesium ate complexes were published by Oshima, in the benzene, pyridine, and thiophene series.[13,16] It is important to mention that in the described protocol using n-Bu$_3$MgLi all three alkyl groups in the magnesium ate complex participate in magnesium halogen exchange reaction. These complexes are also more reactive compared to the ones with salt additives, which allows reactions to be performed at lower temperatures (−30 to 0 °C) with even shorter reaction times.

The commercially available fluorene derivative, 9,9-dioctyl-2,7-dibromofluorene, was tested using regular GRIM. The magnesium halogen exchange of the monomer with either *i*-PrMgCl or *t*-BuMgCl was unsuccessful. The use of either *i*-PrMgCl complexed with a lithium salt or n-Bu$_3$MgLi as the Grignard reagent in the magnesium halogen exchange resulted in the formation of the mono-Grignard reagent, as shown in Scheme 1A.

Table 1 summarizes the reactivity of the different organometallic compounds used for the magnesium halogen exchange reaction. We see that *i*-PrMgCl by itself results in almost no magnesium halogen exchange even after 24 h. Just adding 1 equiv of LiCl to the Grignard solution gives an excellent result of converting 85% of the starting material. The same percent conversion was observed when using *t*-BuMgCl instead of *i*-PrMgCl, but only after double the reaction time. Using LiO*t*Bu as the additive to *i*-PrMgCl results in an even more reactive Grignard complex, converting 90% of the monomer at a shorter reaction time. Unfortunately, some disubstituted compound (7%) is also seen, so the reaction was stopped at this point. Reducing

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Scheme 1. Polymerization Using Different Reagents for Magnesium Halogen Exchange for Polymers (A) Poly(9,9-dioctylfluorene), (B) Poly(*N*-dodecylpyrrole), and (C) Poly(*N*-octyl-2-carbazole)

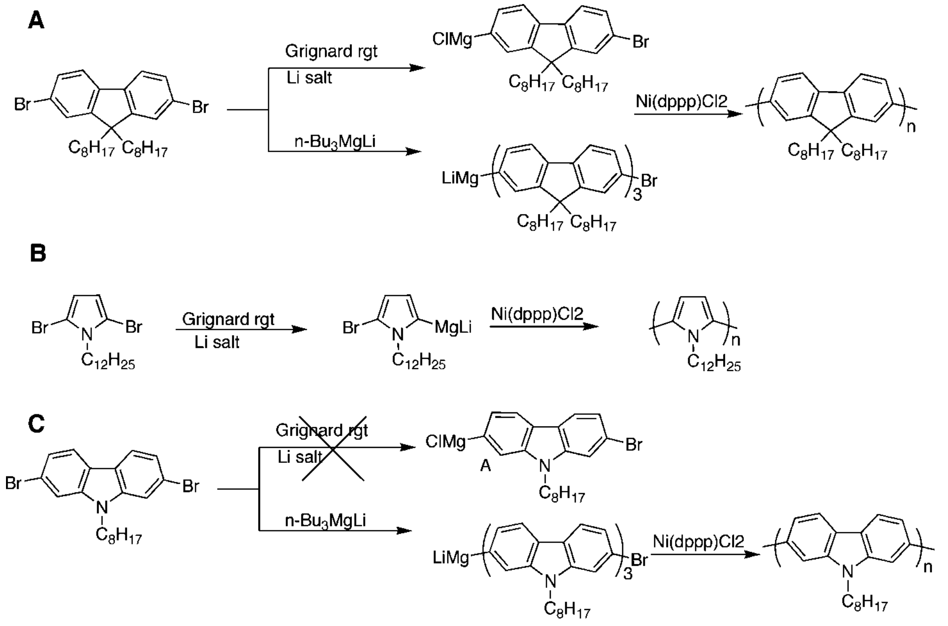

Table 1. Experimental Results for Magnesium Halogen Exchange of 9,9-Dioctyl-2,7-dibromofluorene

reagent	reaction time (h)	mono-	di-	unreacted monomer
i-PrMgCl	24	<5	0	>95
t-BuMgCl	24	<5	0	>95
i-PrMgCl•LiCl	12	85	0	15
t-BuMgCl•LiCl	24	<10	0	90
t-BuMgCl•LiCl[a]	12	85	0	15
i-PrMgCl•LiO*t*Bu	8	90	7	3
n-Bu_3MgLi[b]	4	90	9	1

[a] 15-c-5 used as additive; [*t*-BuMgCl]:[LiCl]:[15-c-5] = 1:1:1. [b] [*n*-Bu_3MgLi]:[DODBF] = 0.35:1.

Table 2. Polymerization Results of 9,9-Dioctyl-2,7-dibromofluorene

entry	conversion (%)	M_n (GPC)	PDI (GPC)	λ_{max} (nm)
1[a]	88	15 000	1.45	388
2[b]	74	5 800	1.66	380
3[c]	85	29 000	1.50	390
4[d]	92	9 700	1.55	384
5[e]		24 000	1.7	373
6[f]		17 800	4.92	

[a] *i*-PrMgCl•LiCl; $[M]_0/[Ni] = 100$, $[M]_0 = 0.2$ mol/L, temperature = 23 °C. [b] *i*-PrMgCl•LiO*t*Bu, $[M]_0/[Ni] = 100$, $[M]_0 = 0.2$ mol/L, temperature = 23 °C. [c] *t*-BuMgCl•LiCl•15-c-5, $[M]_0/[Ni] = 50$, $[M]_0 = 0.2$ mol/L, temperature = 23 °C. [d] *n*-Bu_3MgLi, $[M]_0/[Ni] = 50$, $[M]_0 = 0.2$ mol/L, temperature = 23 °C. [e] Suzuki coupling polymerization reported elsewhere.[11] [f] Yamamoto coupling polymerization reported elsewhere.[18]

the temperature or the reaction time even more may further optimize this option.

In order to speed up the magnesium halogen exchange, *t*-BuMgCl•LiCl was used in conjunction with another additive, crown ether 15-c-5 ([*t*-BuMgCl]:[LiCl]:[15-c-5] = 1:1:1). Additives such as crown ethers and multidentate amines increase the rate of magnesium halogen exchange because they solubilize the lithium salt.[17] The 15-c-5 moiety was used because it forms a stable complex with the lithium ion, which fits inside the cavity.

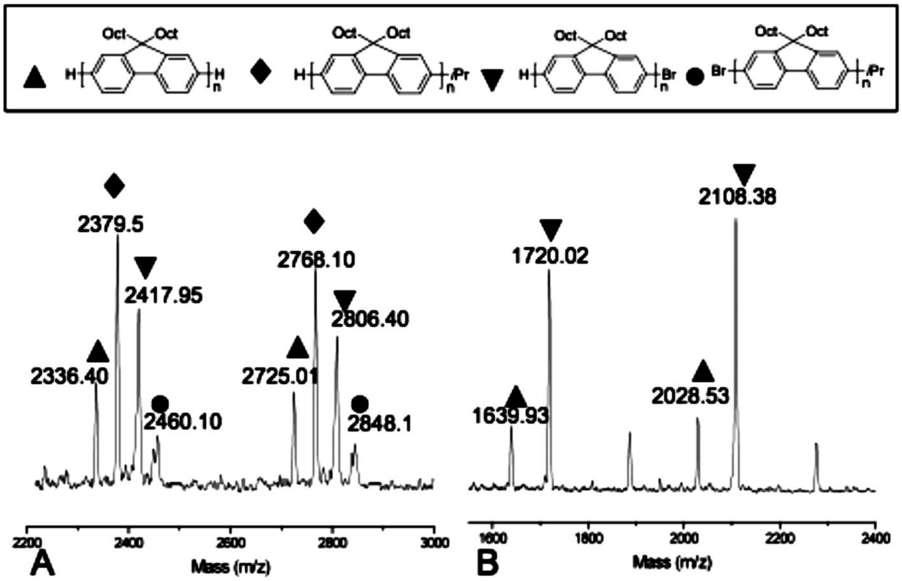

Figure 1. MALDI-TOF MS spectra of poly(9,9-dioctylfluorene): (A) polymer synthesized with *i*-PrMgCl•LiCl; (B) polymer synthesized with *t*-BuMgCl•LiCl•15-c-5.

Table 2 shows the experimental results of polymerization using different Grignard reagents or additives. Samples were periodically taken out and quenched in methanol to follow the conversion of the monomer into the polymer. Polymerization time for all runs was set at 20 min, and we can see that a high conversion rate is observed even at this short reaction time. The conditions used for polymer in entry 3 also show the highest molecular weight polymer, while maintaining a relatively low PDI value. UV−vis absorption data of the different polymers show very similar maxima.

Figure 1 shows the MALDI-TOF MS spectra of polymers synthesized using either *i*-PrMgCl or *t*-BuMgCl and LiCl. We see that the *t*-BuMgCl gives less variety of substituents on the end groups, with H/H and H/Br being the major contributors. The *tert*-butyl cation is more stable compared to the isopropyl cation and does not seem to undergo further substitutions with the remaining halogen, preventing its addition to the polymer.

Universal GRIM was also tested, to a lesser degree, with other monomers that can also produce conjugated polymers that have several potential applications. One of these is polypyrrole (PPy), which is generally prepared by electrochemical and chemical oxidative polymerization methods.[19,20]

The magnesium halogen exchange of 2,5-dibromo-*N*-dodecylpyrrole using either *i*-PrMgCl or *t*-BuMgCl did not suitably generate the mono-Grignard reagent, even after application of heat. The use of *i*-PrMgCl·LiCl as Grignard reagent in the magnesium halogen exchange was sufficient enough and resulted in the formation of the mono-Grignard reagent at very high yields, as seen in Scheme 1B. A polymer with $M_n = 11\,900$ and PDI = 1.4 was obtained upon addition of nickel catalyst. Other additives were not attempted.

Polycarbazoles (PCZ) are another well-known and well-studied class of polymers with good electro- and photoactive properties.[21] The magnesium halogen exchange of 2,7-dibromo-*N*-octylcarbazole with *i*-PrMgCl·LiCl was significantly slower compared to both the fluorene and the pyrrole monomer. Almost no conversion was observed even after 24 h. In contrast, when lithium tributylmagnesate (n-Bu$_3$MgLi) was used for magnesium halogen exchange, the reaction was completed in 5 h at room temperature (Scheme 1C). The yield of polymerization was 50% after 5 h, and a polymer with $M_n = 2600$ and PDI = 1.23 was obtained.

In conclusion, different aromatic and heteroaromatic dibromo compounds were polymerized using a method that was previously applied toward thiophenes and thiophene-based materials.[22] The magnesium halogen exchange step in the reaction was performed using either a Grignard reagent with lithium salt or a magnesium ate complex. Polymers were obtained in high yield, using short reaction times. This method paves the way toward the synthesis of block copolymers using different combinations of monomers. Current research in this area is ongoing.

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Supporting Information Available: Experimental procedures; ^{1}H NMR and MALDI-TOF spectra of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) The Universal Grignard Metathesis Polymerization is the subject of US patent application with publication number US 2008/0146754 filed on Aug 31, 2007.

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