

## Experimental

*Materials.* Lithium chloride, lithium *t*-butoxide, isopropyl magnesium chloride (2M in THF), *t*-butyl magnesium chloride (2M in diethyl ether), *n*-butyl magnesium chloride (2M in THF), *n*-butyl lithium (1.6 M in hexane), and 9,9-dioctyl-2,7-dibromofluorene were purchased from Aldrich and used as received. Tetrahydrofuran was distilled from sodium benzophenone ketyl and collected over molecular sieves. *n*-Bu<sub>3</sub>MgLi was synthesized in anhydrous toluene at -10<sup>0</sup>C as previously reported.

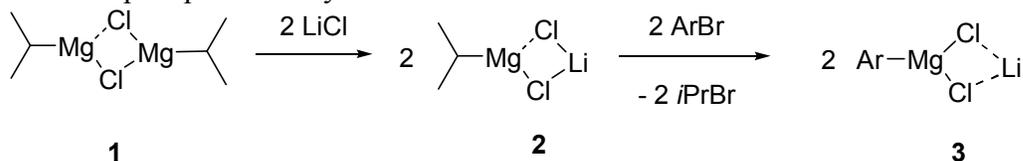
*Synthesis of RMgCl.LiX (R = i-Pr or t-Bu; X = Cl or t-BuO).* A dry 50 mL three-neck flask was flushed with nitrogen and was charged with a 2M solution of *i*-PrMgCl in THF (2.5 mL, 5 mmol) and 5 mL of anhydrous THF. Lithium salt (5 mmol) was added to the reaction flask under nitrogen. The reaction mixture was stirred for 6-8 hrs at room temperature.

*General synthesis of polymers using i-PrMgCl•LiCl as reagent for magnesium halogen exchange.* A solution of dibrominated monomer (5 mmol) in 5 mL of anhydrous THF was added under nitrogen to the previously prepared solution of *i*-PrMgCl•LiCl (5 mmol). The reaction mixture was stirred at room temperature, and monitored by GC-MS. Analysis of the reaction mixture confirmed the formation of monoGrignard reagent in at least 85 % yield. Ni(dppp)Cl<sub>2</sub> (0.02 g, 0.04 mmol) was added to the reaction mixture dissolved in 10 mL anhydrous THF. The polymerization was allowed to proceed for 2-48 h at room temperature followed by quenching of the reaction mixture with methanol. The precipitated polymer was filtered through a thimble and subjected to methanol extraction. The polymer was dried under vacuum for 12 hrs.

*Synthesis of ate complex  $n\text{-Bu}_3\text{MgLi}$ .* Butyl lithium (1.6 M in hexanes, 1.1 mmol) was added to a solution of  $n\text{-BuMgCl}$  (2M in THF, 0.55 mmol) in dry toluene (2 mL) at  $-10^\circ\text{C}$ , under nitrogen. After stirring for 1 h at  $-10^\circ\text{C}$ , a solution of aryl or heteroaryl halide monomer (1.65 mmol in 5 mL dry THF) was added under nitrogen.

*General synthesis of polymers using magnesium ate complex as reagent for magnesium halogen exchange.* A dry 25 mL three-neck flask was flushed with nitrogen and was charged with butyl lithium (1.6 M in hexanes, 1.1 mmol) and a solution of  $n\text{-BuMgCl}$  (2M in THF, 0.55 mmol) in dry toluene (2 mL) at  $-10^\circ\text{C}$ . After stirring for 1 h at  $-10^\circ\text{C}$ , a solution of the di-brominated monomer (0.81 g, 1.65 mmol) in 5 mL of anhydrous THF was added under nitrogen. The reaction mixture was stirred for 1-5 hrs at  $40^\circ\text{C}$  and monitored by GC-MS until such time that  $>80\%$  of the monomer has been converted into the monoGrignard reagent.  $\text{Ni}(\text{dppp})\text{Cl}_2$  (0.01 g, 0.02 mmol) was added to the reaction mixture. The polymerization was allowed to proceed for 0.5 to 6 h at room temperature followed by quenching of the reaction mixture with methanol. The precipitated white polymer was filtered through a thimble and subjected to washing with cold methanol. The polymer was dried under vacuum for 12 hrs.

Addition of lithium chloride additive to isopropyl magnesium chloride enhances its reactivity. This type of very reactive Grignard reagent is known under the generic name of TurboGrignard. Addition of lithium chloride to a Grignard reagent breaks the polymeric aggregates producing a very reactive complex **3** (Scheme 1). The magnesiate character of **3** [ $i\text{PrMgCl}_2\text{Li}^+$ ] may be responsible for the enhanced reactivity of this reagent. This magnesiate is expected to have higher reactivity towards electrophiles, such as nickel phosphine catalysts.



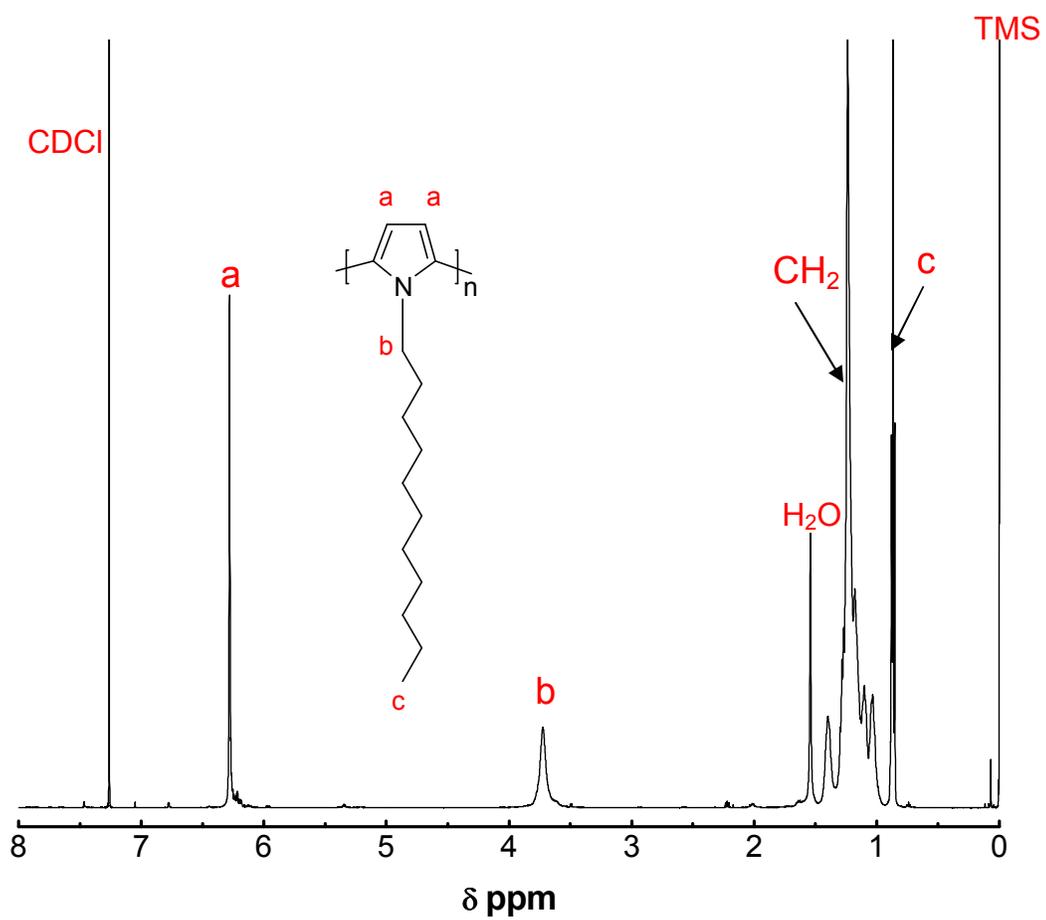
**Scheme 1.** Catalysis of Br/Mg exchange reaction with lithium chloride

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are needed to see this picture.

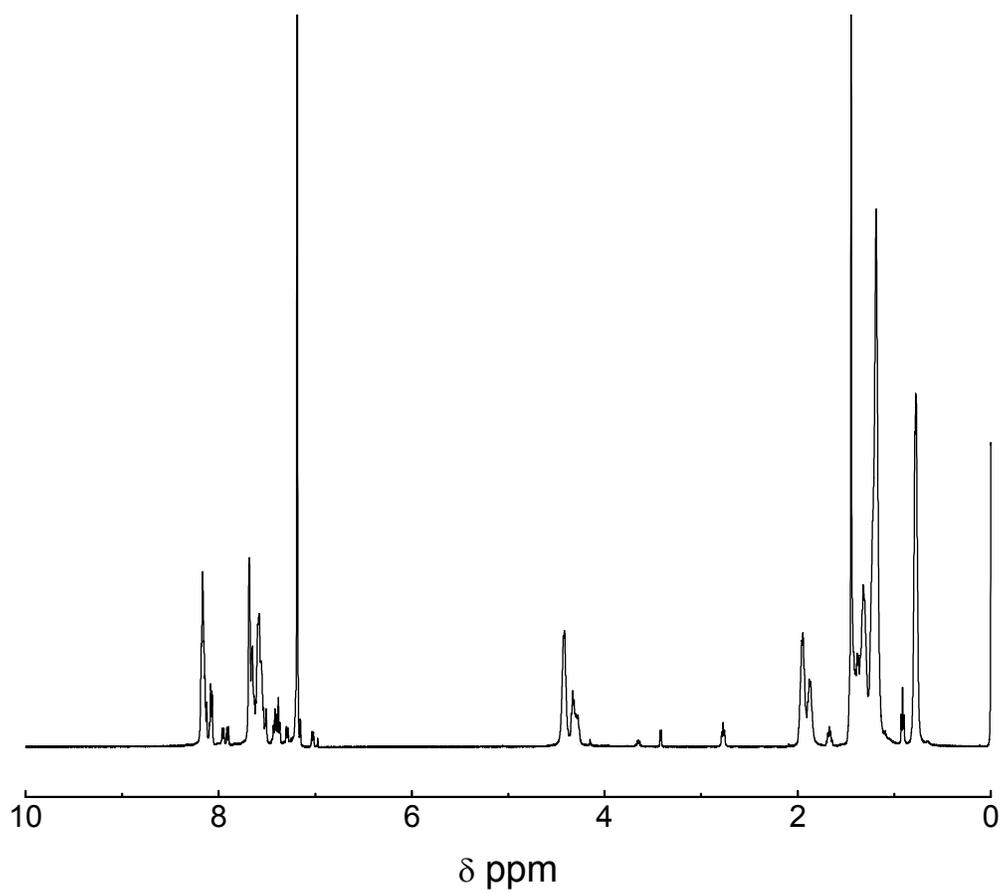
**Figure 1.**  $^1\text{H-NMR}$  of poly(9,9-dioctylfluorene).

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**Figure 2.** MALDI-TOF of poly(9,9-dioctylfluorene) synthesized using different grignard reagents.



**Figure 3.**  $^1\text{H}$  NMR of poly(N-dodecyl pyrrole) synthesized by Universal GRIM with  $i\text{PrMgCl-LiCl}$  and  $\text{Ni(dppb)Cl}_2$  catalyst.



**Figure 4.**  $^1\text{H}$  NMR of poly(carbazole) synthesized by Universal GRIM.