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Chain-Growth Synthesis of Polyfluorenes with Low Polydispersities, Block Copolymers of Fluorene, and End-Capped Polyfluorenes: Toward New Optoelectronic Materials

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ABSTRACT: Here we present the kinetics on the polymerization of poly(9,9-dioctylfluorene) using the Grignard metathesis method (GRIM). By adjusting the reaction conditions, we observed a chain-growth mechanism evidenced by the relatively high molecular weight polymer produced early in the reaction. Well-defined fluorene polymers with average molecular weights of about 10 kDa and with PDI values < 1.2 have been produced. We have also found that under certain conditions end-capping of the polymer chain can be obtained. Using these conditions, we have also been able to synthesize two new block copolymers, poly(9,9-dioctylfluorene)-*b*-poly(3-hexylthiophene) (PF8-*b*-P3HT) and poly(9,9-dioctylfluorene)-*b*-poly(1,4-dioctyloxyphenylene) (PF8-*b*-PPP), that have been produced through chain extension by monomer addition.

Introduction

The drive for better emitters for use in organic light-emitting diodes (OLEDs) remains an important research area, especially as flat-panel, flexible OLED displays have been introduced into the consumer market. While OLED displays show beautiful, vibrant colors and can be more efficient than traditional liquid crystal displays, they can be expensive. Some of the polymer components in red, green, blue (RGB) displays, such as the blue luminescent polymers, can also degrade easily and therefore have short life spans. Perhaps just as interesting is the possibility of all-polymer white lighting, which is important as low-power, energy-efficient organic lighting, and displays are still highly desirable.

Polyfluorenes (PFs) remain one of the most important PLED materials, often showing a strong blue fluorescence stabilized by its rigid, conjugated structure.[1] 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. PF derivatives, including substituted PFs and copolymers, have been developed to fluoresce within the entire range of the visible spectrum.[2,3] However, one disadvantage is that the color of PF-based PLED devices tends to degrade with applied voltage due to interchain excimer formation.[1,4]

The evolution of PF synthetic methods has been discussed previously.[5] PFs are usually synthesized through a variety of polycondensation reactions with metal catalysts, among them Suzuki, Yamamoto, and Stille coupling reactions. Polymerization using these methods usually requires 2−3 days and high temperatures (> 100 °C) to generally yield high molecular weight polymers with broad polydispersities. Consequently, there still exists a need for increased control over the polymer synthesis, which would enable the generation of stable, high-molecular-weight, and degradation-resistant PFs. Recently, both Wang[6] and McCullough[7] reported separately on the use of the Grignard metathesis (GRIM) method to synthesize PFs. The GRIM method is based on a nickel transfer mechanism, which enables chain-growth polymerization.[8,9] This leads to the synthesis of conjugated polymers, with relatively high molecular weight early in the reaction, a narrow molecular weight distribution, and minimized termination reactions.[9−11]

In this paper, we investigate the kinetics of the Grignard metathesis chain growth polymerization of poly(9,9-dioctylfluorene) (PF8), comparing the effects of temperature, catalyst concentration, and time with monomer conversion, molecular weight, and polydispersity. While another report has outlined the chain-growth polymerization of polyfluorene, it was through a different reaction scheme and makes use of an externally added initiator unit.[12] Additionally, we performed chain extension on a PF8 polymer chain to yield block copolymers consisting of (A) fluorene and thiophene and (B) fluorene and phenylene moieties as well as producing end-capped functionalized polymers.

Experimental Section

Materials. [1,3-Bis(diphenylphosphino)propane]dichloronickel(II) (98%) ($Ni(dppp)Cl_2$), isopropylmagnesium chloride−lithium chloride complex solution (1.3 M in tetrahydrofuran), anhydrous hexadecane (≥99%), and 9,9-dioctyl-2,7-dibromofluorene (98%) were purchased from Aldrich Chemical Co., Inc., and used without further purification. Synthesis of 2,5-dibromo-3-hexylthiophene was performed according to the literature. Dry tetrahydrofuran (THF) was obtained from an anhydrous solvent system.

Polymerization Kinetic Experiments. The polymerization of PF8 was performed as previously reported.[7] In a typical experiment, a dry 100 mL three-neck round-bottom flask was flushed with N_2 and charged with 9,9-dioctyl-2,7-dibromofluorene (2.54 g, 5 mmol), hexadecane (internal standard) (0.2 mL), and anhydrous THF (5 mL). A 1.3 M solution of isopropylmagnesium chloride−lithium chloride complex solution in tetrahydrofuran (*i*-PrMgCl·LiCl), was added via a deoxygenated syringe, and the reaction mixture was gently refluxed at 40 °C for at least 8 h. At this time an aliquot (0.1 mL) was taken out and quenched with methanol. The organic phase was extracted in diethyl ether and analyzed by GC-MS to determine the composition of the reaction mixture. The main components of the reaction mixture were 9,9-dioctyl-2-bromofluorene and unreacted 9,9-dioctyl-2,7-dibromofluorene. The concentration of

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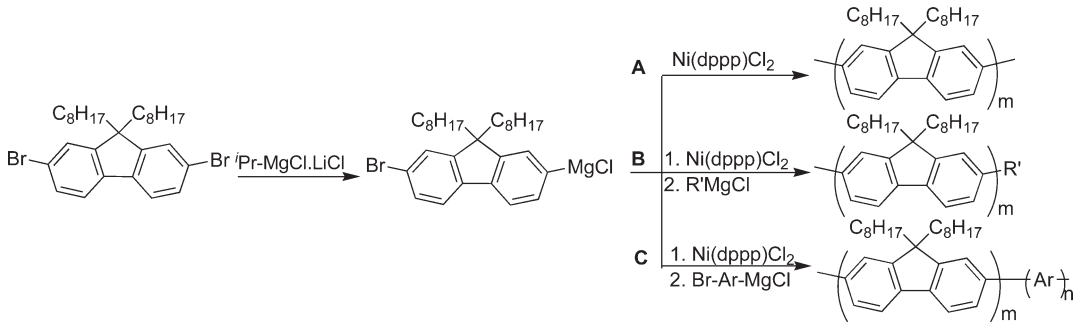
Scheme 1. Synthesis of (A) Poly(9,9-dioctylfluorene), (B) End-Group-Functionalized Poly(9,9-dioctylfluorene), and (C) Block Copolymers of Poly(9,9-dioctylfluorene)



9,9-dioctyl-2-bromofluorene was considered as the initial monomer concentration. The oil bath was then removed, and the reaction mixture was allowed to cool, at which time the solution was further diluted with 43 mL of anhydrous THF and variable amounts of $Ni(dppp)Cl_2$ (0.01−0.04 g, 0.02−0.08 mmol) was added as a suspension in 2 mL of anhydrous THF. After addition of $Ni(dppp)Cl_2$, aliquots (5 mL) were taken at different time intervals, and each was precipitated in methanol (20 mL). From each aliquot, a sample was prepared in diethyl ether (2 mL) and analyzed by GC-MS for the determination of concentration of unreacted monomer. Polymer samples were collected and rinsed with warm acetone, and the molecular weight was measured by GPC.

Chain Extension Experiment for the Synthesis of Poly(9,9-dioctylfluorene)-*b*-poly(3-hexylthiophene). A dry 100 mL three-neck round-bottom flask (A) was charged with 9,9-dioctyl-2,7-dibromofluorene (1.27 g, 2.5 mmol), hexadecane (internal standard) (0.1 mL), and anhydrous THF (3 mL). A 1.3 M solution of *i*-PrMgCl·LiCl in tetrahydrofuran was added via a deoxygenated syringe, and the reaction mixture was gently refluxed at 40 °C for at least 8 h and then diluted with 20 mL of THF. A dry 50 mL three-neck round-bottom flask (B) flushed with N_2 was charged with 2,5-dibromo-3-hexylthiophene (0.815 g, 2.5 mmol) and anhydrous THF (3 mL). A 2 M solution of *t*-BuMgCl (1.25 mL, 2.5 mmol) in diethyl ether (Et_2O) was added via a deoxygenated syringe, and the reaction mixture was allowed to react for 2 h. The concentration of 2-bromo-3-hexylthiophene was determined by GC-MS. $Ni(dppp)Cl_2$ (0.01 g, 0.018 mmol) was added as a suspension in 1 mL of anhydrous THF to flask A. The polymerization was allowed to go for 10 min before 2-bromo-5-chloromagnesium-3-hexylthiophene was added by cannula, and polymerization was continued for another 10 min. Sample aliquots were taken out and precipitated in methanol, collected, and rinsed with warm acetone. The final sample was then quenched in methanol and purified with successive extractions of methanol, acetone, and chloroform.

Analyses. GC-MS analysis was performed on a Hewlett-Packard Agilent 6890-5973 GC-MS workstation. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethylsiloxane with helium as the carrier gas. The following conditions were used for all GC-MS analyses: injector temperature, 250 °C; initial temperature, 70 °C; temperature ramp, 10 °C/min; final temperature, 320 °C. Gel permeation chromatography (GPC) measurements were performed on a Waters 2690 separations module apparatus and a Waters 2487 dual λ absorbance detector with chloroform as the eluent (flow rate 1 mL/min, 35 °C, λ 254 nm) and a series of three Styragel columns (104, 500, 100 Å; Polymer Standard Services). Toluene was used as an internal standard, and calibration based on polystyrene standards was applied for determination of molecular weights. ^{1}H NMR spectra of the polymer solutions in $CDCl_3$ were recorded on a Bruker Avance 500 MHz spectrometer. UV−vis−NIR spectra were measured on polymer solutions in anhydrous chloroform or polymer thin films cast onto 22 mm square cover glass using a UV−vis−NIR spectrophotometer (Varian Cary 5000). Emission spectra for the same samples were then obtained using a Fluorolog TCSPC by HORIBA Jobin Yvon.

Results and Discussion

On the basis of our previous report, we have shown that it is possible to apply a modified Grignard metathesis method in the synthesis of polyfluorenes, through the use of a turbo-Grignard.[7] However, the kinetics of the polymerization was not examined at the time. In this report, we investigated different polymerization conditions and studied their kinetics and were able to synthesize conjugated block copolymers as well as end-group-modified polymers.

Homopolymerization. The PF8 polymer was synthesized as previously reported,[7] wherein 1 mol % of catalyst was used in relation to the amount of monomer. Under these conditions, conversions of 60−90% during the magnesium halogen exchange reaction were observed, as seen in Scheme 1. Temperature was maintained at 40 °C during this step and was allowed to go for at least 8 h. GC-MS measurements revealed that only 2-bromo-7-chloromagnesio-9,9-dioctylfluorene and unreacted 2,7-dibromo-9,9-dioctylfluorene were present in the reaction mixture. The mixture was further diluted, and $Ni(dppp)Cl_2$ was added to start polymerization. Samples were taken out periodically to follow the polymerization and for kinetic calculations.

Figure 1 shows the kinetics of the fluorene polymerization at variable temperatures, while maintaining the $Ni(dppp)Cl_2$ catalyst and monomer concentration. The linear increase in the plot of the logarithm of monomer concentration vs time indicates that the concentration of reactive centers is constant, with no rapid increase or decrease.[10] When the line curves upward, it indicates that the reactive centers are increasing: this may be caused by the initial poor solubility of the catalyst added into the reaction mixture. A decreasing curve, on the other hand, indicates the decrease in the concentration of reactive centers, usually caused by chain termination.

Increasing the temperature usually increases the reaction rate. As seen in the Figure 1, the slope of the initial linear part of the polymerization is increasing with increasing temperature. Since the slope is proportional to the rate of the polymerization, the initial rate of the reaction can be extracted from the slope of linear part of the semilogarithmic plot. It was observed that polymerization at 0 °C was best able to maintain the linearity of the semilogarithmic kinetic plot through the first 10 min, so this temperature was used for the rest of the experiments that were performed at constant monomer concentration and variable $Ni(dppp)Cl_2$ concentration.

In the next experiments, the effect of varying the ratio of catalyst to monomer concentration was examined. Figure 2A shows that the initial polymerization reaction rate increases when increasing the Ni(dppp)Cl_2 concentration from 0.5 to 2 mol %, which follows reports of first-order dependence on the catalyst in the GRIM mechanism.[13] The plots show a linear increase initially and then leveled off with time, indicating an increasing amount of chain termination. The semilogarithmic kinetic plots were seen to be linear up to about 40% conversion, which occurred during the first 10 min. Thereafter, the nonlinearity of semilogarithmic kinetic plots indicate the presence of chain termination reactions, which could be due to the formation of large polymer aggregates mixed with unassociated or very weakly associated polymer chains.[14] Once polymer aggregation occurs, the reactive centers become inaccessible, resulting in chain termination.

Figure 2B shows that the molecular weights of the polymer samples taken at different time intervals linearly increase with time and conversion. However, using 1.0 mol % of Ni(dppp)Cl_2 gave the most linear plot, which could indicate quasi-"living" conditions during the initial period of polymerization. GPC traces of the PF8 polymer samples taken during these experiments occasionally show a multimodal composition, which is attributed to the difficult purification of the small amount of material (aliquots) taken during the kinetic study. Since the fluorene monomer was relatively insoluble in methanol, acetone was utilized to dissolve the monomer and the shorter oligomers, but the longer oligomers still remained. These were harder to remove because its solubility was very similar to that of the polymer. Because of the larger amount of the final sample obtained after the complete quenching of the polymerization, it was easier to purify by means of successive extractions with methanol, acetone, and chloroform. PDI values remained low (< 1.2), even for samples taken early in the reaction, which indicated that there was little chain-transfer occurring during the initial stages of the reaction. We also see that relatively high molecular weight was obtained early in the polymerization. Though the M_n vs conversion plot shows a lower than expected molecular weight if it were a truly living polymerization, recent work by Rawlins et al. on the mechanism of GRIM has shown that other factors can control the molecular weight, and not just the amount of Ni catalyst.[15] This includes the equilibrium between the free or diffusing Ni(0) and the "associated pair" between the Ni and the growing thiophene chain. However, when comparing the PF8 synthesis to the Grignard metathesis method (GRIM) for thiophene derivatives,[16] we observed that the two systems showed similar kinetic behavior during synthesis and conclude that PF8 must be following a chain growth mechanism as well.

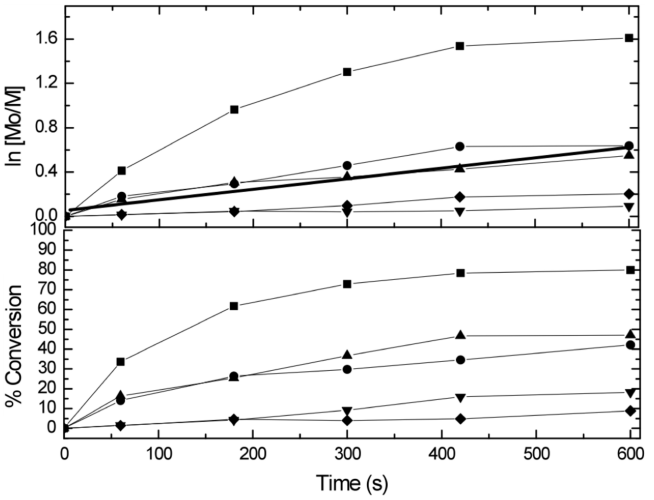


Figure 1. Conversion and first-order kinetics of monomer consumption vs time plots for 2-bromo-7-chloromagnesium-9,9-dioctylfluorene Grignard metathesis polymerization at variable temperatures with Ni(dppp)Cl_2 at maintained at 1 mol % (■, 40 °C; ●, 25 °C; ▲, 0 °C; ◆, −10 °C; ▼, −30 °C). Line provided for 0 °C points as a guide to the eye.

End-Capping. The reaction was also assessed for its potential to selectively end-cap the polymer as seen from Scheme 1. The polymerization temperature was maintained at 0 °C, and 1 mol % of the Ni(dppp)Cl_2 catalyst was used. The polymerization reaction was set up as described in the previous section, and kinetic samples were taken at different times. At different time points (7, 10, and 15 min), a set amount (10 mL each) of the reaction mixture was then transferred into a separate flask that contained a different Grignard reagent from the one previously used in the metathesis reaction (step 1 in Scheme 1). Each separate reaction was then stirred vigorously under N_2(g) for

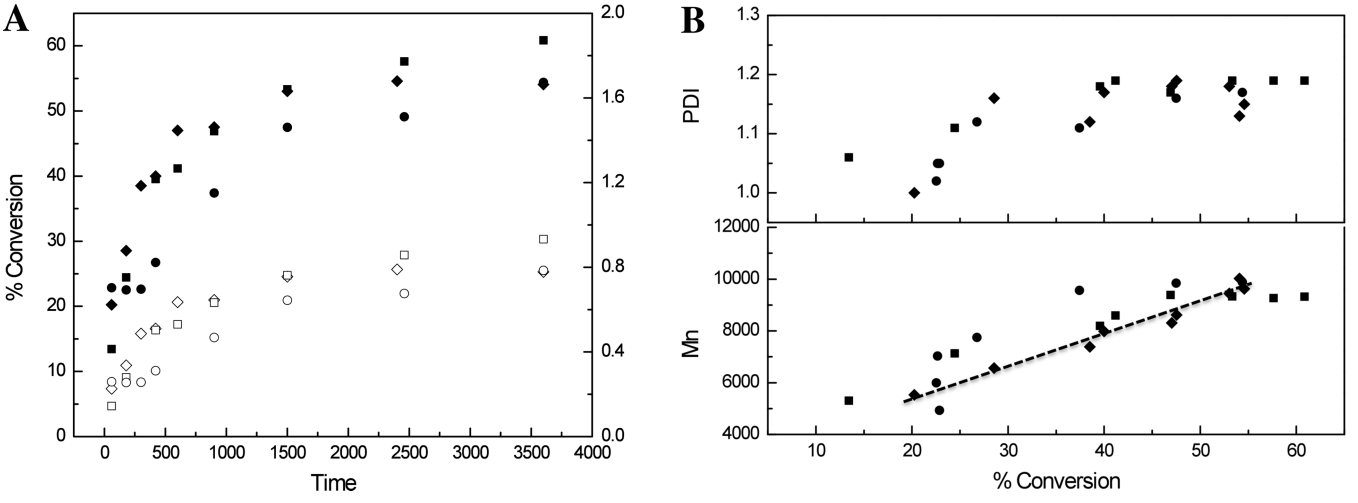


Figure 2. (A) Conversion (filled symbols) and first-order kinetics of monomer consumption (open symbols) vs time plots and (B) dependence of molecular weights and polydispersities on conversion for 2-bromo-7-chloromagnesium-9,9-dioctylfluorene Grignard metathesis polymerization at variable Ni(dppp)Cl_2 concentrations (●, 0.5 mol %; ◆, 1.0 mol %; ■, 2 mol %). Dotted line connects the points for 1.0 mol % catalyst.

another 5−10 min, after which all reactions were quenched in methanol.

^{1}H NMR (500 MHz) was used to assess the percentage of end-capped polymer at each sample time, as seen in the Supporting Information (Figure S1), while Table 1 contains a summary of results obtained from end-capping. Moderate end-capping success in both P1 and P2 samples correlates to the polymerization still being its quasi-"living" phase (through the first 10 min). Large-scale termination reactions would not have occurred, thus allowing newly introduced Grignard reagents to attach at the terminal end of the polymer. However, the end-capping percentages were beneath expectations, suggesting only mild capping potency of R′-MgBr in the nickel-catalyzed reaction. We surmise that the P3 samples showed even lower end-capping potential since the reaction was its "living" point at 15 min. Larger amounts of termination started to occur, thereby reducing the number of viable chains for end-capping.

Block Copolymerization. Although conjugated block copolymers have been reported before, these was usually prepared using multistep procedures, with each step requiring the purification of the polymer obtained.[17−19] On the basis of the results obtained for homopolymerization of PF8, it seemed feasible that diblock copolymers containing PF8 could be obtained by means of simple chain extension, as outlined in part C of Scheme 1. PF8 was synthesized using 1 mol % of Ni(dppp)Cl_2, and polymerization temperature was maintained at 0 °C. We proceeded with the sequential monomer addition by adding 2-bromo-5-chloromagnesio-3-hexylthiophene to the active polymer chains of PF8, and the reaction temperature was allowed to rise to room temperature. After an additional 10 min, the entire solution was then quenched in methanol to yield a block copolymer consisting of 40 mol % poly(9,9-dioctylfluorene) and 60 mol % poly(3-hexylthiophene) (PF8-*b*-P3HT) that retains a low PDI value of 1.23. The ^{1}H NMR spectra obtained for this polymer is shown in Figure S2. To our knowledge this is the first reported one-pot synthesis of a diblock copolymer consisting of fluorene and thiophene units. A variety of polymer compositions can be prepared by taking out sufficient aliquots during the course of the reaction.

Table 1. Summary of Results from End-Capping the Polymer with Methyl-MgBr and Phenyl-MgBr

polymer sample	time (min)	% CH_3 end-capped (NMR)	% Ph end-capped (NMR)
P1	7	50	40
P2	10	50	30
P3	15	20	30

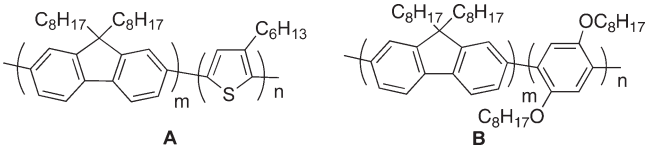


Figure 3. Structures of block copolymers synthesized by chain extension.

Figure S3 shows the gel permeation chromatography traces of the PF8 homopolymer and PF8-*b*-P3HT block copolymer samples. We see an efficient catalyst transfer from the fluorene polymer chains to the thiophene monomer indicated by the increase in MW of the block copolymer obtained. A previous report by Yokozawa, which was based on a similar methodology, outlined the synthesis of block copolymers of polythiophene and poly(*p*-phenylene) (P3HT-*b*-PPP).[20] They hypothesized that the successful block copolymerization of the two units may be accounted for by their π-donor ability. Thus, the high efficiency of intermolecular catalyst transfer from the fluorene to thiophene units may be attributed to greater attraction of the catalyst to the thiophene unit. Another block copolymer, PF8-*b*-PPP, was synthesized in a similar manner as PF8-*b*-P3HT. A sample ^{1}H NMR spectra is shown in Figure S4. However, a higher PDI value was obtained for PF8-*b*-PPP, with the GPC trace showing a bimodal peak (Figure S5, polymer 1). This could be due to a less efficient catalyst transfer from fluorene to phenylene. Studies on the synthesis of block copolymers of PPP and P3HT have shown that the order of monomer addition is crucial in the synthesis of block copolymers.[20,21] On the basis of these studies, we hypothesized that the synthesis of a well-defined PF8-*b*-PPP polymer could be obtained by reversing the order of monomer addition—starting with polymerization of phenylene and then chain extension with fluorene. This was attempted, and we see the disappearance of the bimodality in the GPC trace with a lower PDI value of 1.45 (Figure S5, polymer 2). Further optimization regarding polymerization conditions for phenylene could lead to higher molecular weight polymers and is beyond the scope of this study.

The absorption and photoluminescence (PL) spectra of the synthesized polymers were also obtained, in both dilute solution ($CHCl_3$) and solid state (thin film), and are shown in the Supporting Information. For the PF8 homopolymer, we see the absorbance maxima at 380 nm for both solution and thin film. The P3HT peaks are seen at 450 and 550 nm for solution and thin film, respectively. Using the values obtained for PF8 absorption as the excitation wavelength, the PL spectra showed fluorene emission at around 420 nm for the solution and 435 nm in the thin film. For the PF8-*b*-P3HT block copolymer sample, the energy transfer and charge trapping from one polymer to the other block are observed and lead to emission from both polymer units in the PL process.[22−25] The actual spectra show contributions from both polymer blocks—the emission ∼400 nm is attributed to the PF8 block, while the peak at ∼560 nm (solution) and ∼650 nm (thin film) is from the P3HT. The increased intensity of the P3HT block's emission compared to a P3HT homopolymer is related to an efficient intramolecular excitation energy transfer (Förster transfer).[23] P3HT has very low intensity emissions in thin films, primarily attributed to the efficient packing of the polymer.[26] The PF8-*b*-PPP block copolymer sample was also analyzed in the same way and showed contribution of both polymers in both solution and thin film samples. Future work could include the analysis of the PL performance of the polymer in actual OLED or OFET devices.

Table 2. Comparison between PF8 Homopolymer and Block Copolymer Samples

sample	mol % PF8	M_n	PDI	Abs λ_{max} soln	Abs λ_{max} film	Em λ_{max} soln	Em λ_{max} film
PF8	100	4830	1.09	380	380	420	435
PF8-*b*-P3HT (A)	40	7760	1.23	380, 450	380, 550	420, 560	435, 650
PF8-*b*-PPP (B)	20	9210	2.01	340, 380	340, 390	420	450
PPP-*b*-PF8	10	5610	1.45				

Conclusions

The kinetics of the synthesis of poly(9,9-dioctylfluorene) using the Grignard metathesis (GRIM) method was examined, and it was found that the polymerization follows a chain-growth mechanism. This mechanism is evidenced by the relatively high molecular weight polymer produced early in the reaction and a linear semilogarithmic kinetic plot observed in the first 10 min of the polymerization. The effect of temperature and catalyst-to-monomer ratio on the polymerization rate was also studied. Analysis of the polymerization kinetic data gave rise to conditions that led to the production of new materials—first, through end-capping of PF8 and, second, through polymer chain extension that led to the synthesis of the block copolymers PF8-*b*-P3HT and PF8-*b*-PPP. This method opens up the possibility of making a variety of new optoelectronic polymers by either simple end-capping that leads to end-functionalized polymers or synthesizing other conjugated block copolymers.

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Supporting Information Available: Representative ^{1}H NMR plots, GPC traces, UV−vis absorption, and emission spectra of the homopolymer and block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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