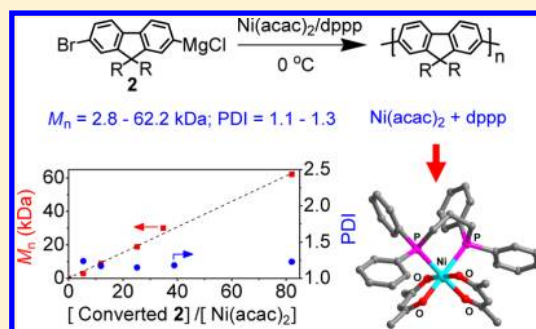


Controlled Synthesis of Polyfluorenes via Kumada Catalyst Transfer Polycondensation with $\text{Ni}(\text{acac})_2/\text{dppp}$ as the CatalystAiguo Sui,^{†,‡} Xincui Shi,[†] Shupeng Wu,^{†,‡,§} Hongkun Tian,[†] Yanhou Geng,^{†,*} and Fosong Wang[†][†]State Key Laboratory of Polymer Physics and Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China[‡]Graduate School of Chinese Academy of Sciences, Beijing 100049, P. R. China

S Supporting Information

ABSTRACT: A new catalyst system, i.e., nickel acetylacetonate/1,3-bis(diphenylphosphino)propane ($\text{Ni}(\text{acac})_2/\text{dppp}$), was explored to catalyze the Kumada catalyst transfer polycondensation (KCTP) of three fluorene monomers with different substituents at 9-position. The “living” nature of the polymerization was confirmed by polymerization kinetic studies, “monomer addition” experiment and block copolymerizations. As a result, poly(9,9-dioctylfluorene)s (PF8s) with the number-average molecular weights (M_n s) in the range 2.8–62.2 kDa and polydispersity indices (PDIs) of ~ 1.20 were successfully synthesized in a controlled manner. The syntheses of fluorene-fluorene and fluorene-thiophene diblock copolymers with M_n s up to 46 kDa were also demonstrated. A complex, i.e. $\text{Ni}(\text{dppp})(\text{acac})_2$, with an octahedral coordination geometry was isolated and confirmed by X-ray crystallographic analysis. The polymerization experiments indicated that the in situ formed $\text{Ni}(\text{dppp})(\text{acac})_2$ should be the active catalyst. To the best of our knowledge, this is the first report on the controlled synthesis of polyfluorenes (PFs) via KCTP.



■ INTRODUCTION

Conjugated polymers (CPs) are of particular research interest in past two decades due to their applications in printable optoelectronic and electronic devices.^{1–3} They are usually synthesized by transition metal catalyzed polycondensations,⁴ which usually require 2–3 days and result in the CPs with uncontrollable molecular weights (MWs) and large PDIs. However, the optoelectronic properties of CPs often depend on their structural parameters such as MWs, chain ends and compositions.^{5–9} Therefore, it is fundamentally and practically important to realize the controlled synthesis of CPs by developing new polymerization protocols.

Nowadays, the KCTP has become a powerful tool in the synthesis of well-defined CPs.^{10–13} An attractive feature of this protocol is that the catalyst species undergo an efficient intramolecular transfer, facilitating the polymerization to follow a chain-growth mechanism. Nevertheless, so far it is mainly focused on the controlled synthesis of polythiophenes (PThs),^{14–23} polyphenylenes (PPs),²⁴ polypyrroles (PPys),²⁵ polypyridines (PPds),²⁶ and poly(bithienylmethylene)s (PBTMs).²⁷ While monomers with a longer length, such as fluorene,^{28–30} carbazole,²⁹ and oligothiophenes,³¹ were used, the MWs and PDIs of afforded polymers were hardly controlled due to the presence of chain transfer and chain termination. Taking polyfluorenes (PFs) as example, we first demonstrated that KCTP is also suitable for the synthesis of PF8s in 2008.²⁸ Later, McCullough et al. also synthesized PF8s in a similar process except that a different route for the monomer preparation was employed.²⁹ Unfortunately, the MWs of

afforded PF8s were poorly controlled with relatively large PDIs (1.4–1.8), which may be resulted from the inefficient intramolecular catalyst transfer. Further investigations by McCullough revealed that the polymerization showed a “quasi-living” feature during the initial periods, and PF8s with lower PDI (~ 1.2) were synthesized.³⁰ However, the M_n s of PF8s were ≤ 10 kDa and hardly controlled by feed ratio of the monomer to the catalyst. Recently, McNeil et al. demonstrated that a NHC-Pd catalyst could realize the KCTP of phenylene and thiophene monomers.³² However, both chain termination and reinitiation occurred in the polymerization of fluorene monomer. From all above discussion, the controlled KCTP of fluorene monomers has not been realized yet.

Yokozawa et al. have reported the Pd-catalyzed Suzuki–Miyaura catalyst transfer polycondensation for the synthesis of PF8s with controlled MWs and low PDIs with a special three-coordinate Pd-complex as catalyst.^{33,34} McNeil’s recent studies also showed that the structures of ligands have noticeable effects on the polymerization mechanism of the KCTP.^{35,36} These studies imply that the controlled synthesis of PFs might be achieved by finely tuning the structure of the ligand of the Ni catalyst. Recently, Ananikov et al. showed that $\text{Ni}(\text{acac})_2$ is a better catalyst precursor than NiCl_2 and $\text{Ni}(\text{OAc})_2$ for coupling reactions. They found that 2 equiv of phosphine ligands could coordinate with $\text{Ni}(\text{acac})_2$ to form a complex with an

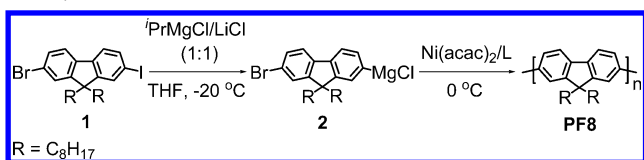
Received: May 8, 2012

Revised: June 15, 2012

Published: June 22, 2012

elongated-octahedral coordination geometry.³⁷ This indicated that acac may play an important role in the catalytic cycle. Inspired by this achievements, we studied the polymerizations of fluorene monomers with Ni(acac)₂/phosphine ligands as the catalysts, and found that the Ni(acac)₂/dppp was a promising catalyst for the controlled synthesis of PFs via KCTP. The PF8s with the *M_n*s in the range of 2.8–62.2 kDa and PDIs of ~1.20 were synthesized (Scheme 1). A series of PFs-based block polymers with low PDIs were also demonstrated. To the best of our knowledge, this is the first report on the controlled KCTP of fluorene monomers.

Scheme 1. Synthesis of PF8s with Ni(acac)₂/L as the Catalyst



RESULTS AND DISCUSSION

To screen the ligands, the polymerizations of 2-bromo-7-chloromagnesio-9,9-dioctylfluorene (**2**) were conducted with triphenylphosphine (PPh₃), 1,2-bis(diphenylphosphino)ethane (dppe), dppp or 1,1'-bis(diphenyl-phosphino)ferrocene (dppf) as the ligand. The ratio of Ni(acac)₂/phosphine ligand was kept at 1/1. As shown in Table 1 (entry 1–4), dppp was the best

Table 1. Polymerization of **2** with Ni(acac)₂/L as the Catalyst^a

entry	L	Ni(acac) ₂ /L	<i>M_n</i> (kDa) ^b	PDI ^b	yield ^c (%)
1	PPh ₃	1/1	6.6	1.60	73
2	dppe	1/1	22.3	1.40	70
3	dppf	1/1	no polymer	—	—
4	dppp	1/1	30.1	1.18	75
5	dppp	1/0	no polymer	—	—
6	dppp	1/0.8	no polymer	—	—
7	dppp	1/1.02	29.5	1.22	76
8	dppp	1/1.2	27.9	1.36	72
9	dppp	1/2	29.3	1.45	71

^aAll polymerizations were carried out at 0 °C for 30 min in the presence of 1 equiv LiCl with [2]₀ = 0.05 mol/L and Ni(acac)₂/L of 2.0–2.2 mol % to **2**. ^bEstimated by GPC with polystyrene as the standard and THF as eluent. ^cCalculated according to **2**.

ligand in terms of *M_n*s and PDIs of the obtained polymers. It was also found that ≥1 equiv dppp to Ni(acac)₂ was necessary to obtain the polymeric products, but larger PDIs were observed when more dppp was used (Table 1, entry 4–9). Therefore, a Ni(acac)₂/dppp ratio of 1/1.02 was used in the following experiments.

The conversions of **2** and *M_n*s of PF8s at different polymerization time were measured by gas chromatography–mass spectroscopy (GC–MS) and gel-permeation chromatography (GPC), respectively. As shown in Figure 1a, the polymerization went on very fast, and was over in 10, 6, and 3 min, respectively, when 1.1, 2.1, and 4.2 mol % of Ni(acac)₂/dppp were used. In the whole polymerization process, *M_n*s of PF8s were linear to the conversions of **2** with PDIs of 1.1–1.3 (Figure 1b). The polymerizations with different amounts of

catalysts were also conducted and the data are listed in Table 2. The *M_n*s varied in the range of 2.8–62.2 kDa along with the PDIs ≤ 1.25, and the yields were up to 80%. The low yield of PF8 with 11 mol % catalyst is attributed to the loss in the precipitation process due to the low *M_n* of the product. Moreover, as shown in Figure 1c, the *M_n*s of the resulting polymers were a linear function of [converted **2**]/[Ni(acac)₂]. Accordingly, GPC profiles shifted to the high MW region with a decrease of the catalyst (Figure 1d). Generally, GPC measurements overestimate the MWs of CPs because of their more rigid chain structures compared to the polystyrene standard. Recently, we have successfully synthesized mono-disperse PF8s up to 64-mer,³⁸ which enables us to calibrate the *M_n*s of the current PF8s (the calibration curve please see Figure S1, Supporting Information). The calibrated *M_n* was recorded as *M_n*['], which is also in proportion to [converted **2**]/[Ni(acac)₂] (Figure 1c). In addition, *M_n*['] is very close to the calculated *M_n* (*M_n*^{cal}, solid line in Figure 1c) based on the equation *M_n*^{cal} = 388.6 × [converted **2**]/[Ni(acac)₂] by assuming that the polymerization follows the living mechanism. All above results indicate the “living” nature of the polymerization, like those for PThs,^{14–23} PPs,²⁴ PPys,²⁵ PPds,²⁶ and PBTMs.²⁷

The matrix-assisted laser desorption ionization time-of-flight (MALDI–TOF) mass spectrum and ¹H NMR spectrum of the PF8 (*M_n* = 8.9 kDa, PDI = 1.17) prepared with 6.6 mol % Ni(acac)₂/dppp as the catalyst (Table 2, entry 2) are showed in the Figure 2. The sample was purified by precipitation in methanol and then Soxhlet extraction with acetone for completely removing the residual monomers. In the MALDI–TOF mass spectrum, only one series of peaks corresponding to Br/H terminated polymer chains are observed, and the *m/z* values can be accurately expressed as 388.6 *n* (repeat unit) + 79.9 (Br) + 1.0 (H). In the ¹H NMR spectrum, the signals at 7.3–7.4 and 7.4–7.5 ppm are assigned to the protons at the H-ends (H_{1–3}) and Br-ends (H_{4,5}), respectively.³⁹ The integral ratio of H_{1–3} to H_{4,5} is about 3:2, which further confirms the PF8 chains are Br/H terminated. This indicates that all of Ni catalysts would be transferred selectively to the polymer propagating ends without reductive elimination from polymer chains, which is consistent with the KCTP mechanism proposed by Yokozawa.¹⁶ Otherwise, polymers with Br/Br chain-ends should be observed, like the previous reports on PF8s with Ni(dppp)Cl₂ as the catalyst.^{28,29} All of these results are consistent with the “living” nature of the polymerization with Ni(acac)₂/dppp as the catalyst.

According to the reference, the properties of PFs can be tuned by modulating the substituents at 9-position.^{40,41} To verify the versatility of the current catalyst system for the controlled synthesis of PFs, the KCTP of other two fluorene monomers **4** and **6** with triphenylamine and phenyl substituents at 9-position, respectively, was also conducted (Scheme 2). As shown in Table 3, the *M_n*s could also be controlled by tuning the feed ratio of monomer to the catalyst Ni(acac)₂/dppp. Meanwhile, the PDIs of the obtained PFs are around 1.3. These results indicate that the current catalyst is suitable for the controlled synthesis of PFs with various substituents at 9-position.

To further confirm the “living” nature of the KCTPs of the fluorene monomers, “monomer addition” experiment and block copolymerizations were carried out. The “monomer addition” experiment was conducted using 4.2 mol % Ni(acac)₂/dppp as the catalyst. After the complete consumption of **2**, another

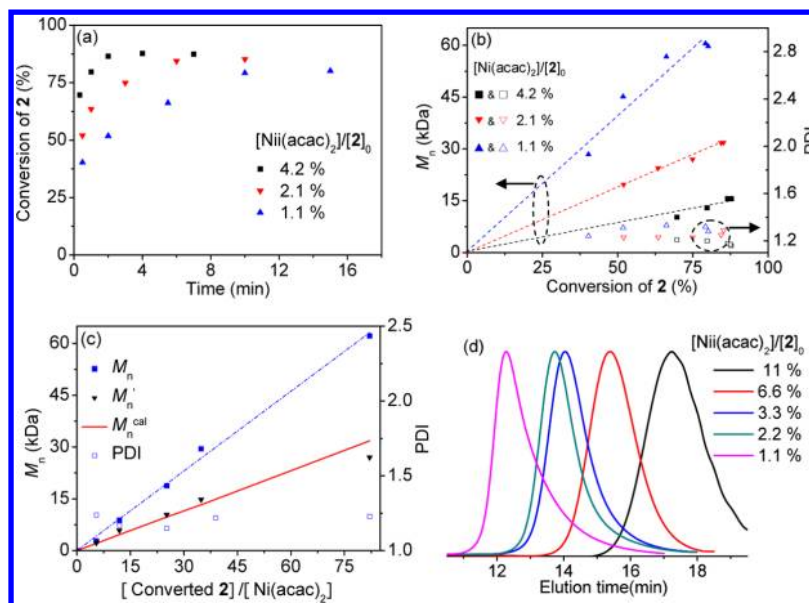


Figure 1. (a) Conversion of **2** versus time. (b) M_n and PDI versus the conversion of **2**. (c) M_n , calibrated molecular weight (M_n'), calculated molecular weight (M_n^{cal}) and PDI versus $[\text{converted } 2]/[\text{Ni}(\text{acac})_2]$. (d) GPC elution curves of PF8s prepared with different $[\text{Ni}(\text{acac})_2]/[2]_0$. M_n is measured by GPC with polystyrene as the standard and THF as eluent. M_n' is calculated according to the calibration curve in Figure S1, Supporting Information. M_n^{cal} is calculated based on $[\text{converted } 2]/[\text{Ni}(\text{acac})_2]$ by assuming that the polymerization follows living mechanism. All polymerizations were carried out at 0 °C with $[2]_0 = 0.05$ mol/L. For parts c and d, the polymerization time was 30 min.

Table 2. Polymerization Results of **2 with Different Amounts of $\text{Ni}(\text{acac})_2/\text{dppp}$ as the Catalyst^a**

entry	$[\text{Ni}(\text{acac})_2]/[2]_0$ (mol %)	M_n^b (kDa)	PDI^b	yield ^c (%)
1	11	2.8	1.24	55 ^d
2	6.6	8.9	1.17	79
3	3.3	18.8	1.15	74
4	2.2	29.5	1.22	76
5	1.1	62.2	1.23	80

^aAll polymerizations were carried out at 0 °C for 30 min in the presence of 1 equiv LiCl with $[2]_0 = 0.05$ mol/L and $\text{Ni}(\text{acac})_2/\text{dppp}$ ratio of 1/1.02. ^bEstimated by GPC with polystyrene as the standard and THF as eluent. ^cCalculated according to **2**. ^dThe low yield is attributed to the loss in the precipitation process due to the low M_n of the product.

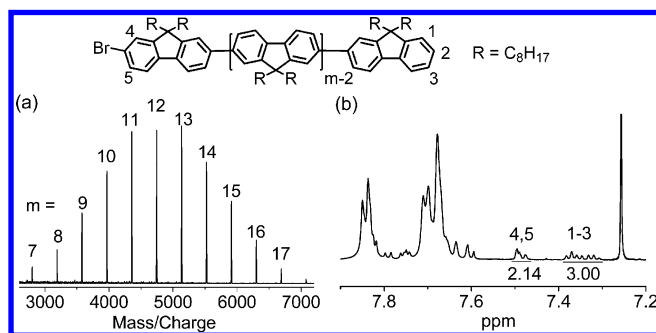


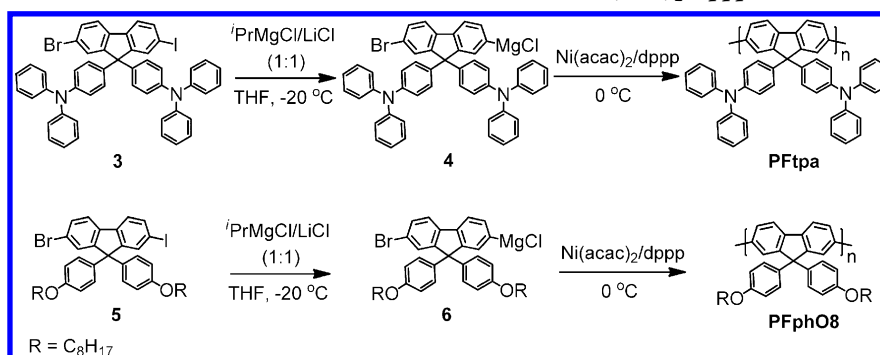
Figure 2. MALDI-TOF mass spectrum (a) and ^1H NMR spectrum (b) of PF8 ($M_n = 8.9$ kDa, $\text{PDI} = 1.17$).

equal amount of **2** was added. As shown in Figure 3a, the unimodal GPC profile shifted to the higher MW region (from 14.1 kDa to 28.5 kDa), and the PDI of the polymer was still kept at ~ 1.20 . This result is consistent with the “living” nature of the KCTP of **2** with $\text{Ni}(\text{acac})_2/\text{dppp}$ as the catalyst.

Block copolymerization for preparing copolyfluorene PFphO8-*b*-PFtpa was first carried out (Scheme 3a). As

shown in Figure 3b, the copolymerization in the order of **6** and then **4** yielded a block copolymer with an unimodal GPC profile, and the M_n increased from 9.5 kDa of the PFphO8 block ($\text{PDI} = 1.25$) to 18.2 kDa of the block copolymer along with a PDI of 1.31. Fluorene-thiophene diblock copolymers (PF8-*b*-P3HTs) with different block ratios were also successfully synthesized in a well-controlled manner as shown in Scheme 3b. M_n s and PDIs of the PF8 blocks and PF8-*b*-P3HTs are listed in Table 4. PF8-*b*-P3HTs are denoted as *FmTn*, in which F and T represent fluorene and thiophene unit, respectively, and m and n are the numbers of fluorene and thiophene units, respectively. All PF8 blocks and PF8-*b*-P3HT diblock copolymers exhibited unimodal GPC profiles (Figure 4a and Figure S2 (Supporting Information)) and PDIs ≤ 1.30 even for F34T74 with M_n up to 46.2 kDa, which indicates a successful block copolymerization in broad MW range. While according to McCullough’s report, the copolymerization with $\text{Ni}(\text{dppp})\text{Cl}_2$ as the catalyst only allowed the synthesis of PF8-*b*-P3HTs with $M_n \leq 10$ kDa.³⁰ The compositions of the afforded block copolymers were determined from ^1H NMR spectrum. Taking F19T71 as an example (Figure 4b; for others, please see Figure S3, Supporting Information), the signals at 7.45–7.50 and 7.55–7.90 ppm are assigned to $\text{H}_{1,2}$ in Br-terminated PF8 chain ends and other aromatic protons H_{3-12} in PF8 block.³⁹ From the integral ratio of H_{3-12} to $\text{H}_{1,2}$ (114:2), the number of fluorene units m was estimated to be 19. The signals at 1.9–2.3 and 2.6–2.9 ppm are assigned to the methylene protons (H_a and H_b) next to the fluorene units in the PF8 block and the thiophene rings in the P3HT block, respectively. The ratio of fluorene and thiophene units (*m*:*n*) was calculated as 21:79. Accordingly, the actual number of thiophene units (*n*) is 71. These *m* and *n* values are very close to those calculated based on $[\text{converted } 2 \text{ and } 7]/[\text{Ni}(\text{acac})_2]$, which are 19 and 68, respectively.

According to Ananikov’s report, 2 equiv of monodentate phosphine ligand PMe_2Ph could coordinate with $\text{Ni}(\text{acac})_2$ to

Scheme 2. Synthesis of PFs with Different Substituents at 9-Position with Ni(acac)₂/dppp as the CatalystTable 3. Polymerization Results of Monomers 4 and 6 with Different Amounts of Ni(acac)₂/dppp as the Catalyst^a

entry	monomer	[Ni(acac) ₂]/[M] ₀ (mol %)	M _n ^b (kDa)	PDI ^b	yield ^c (%)
1	4	6.5	8.8	1.28	59
2	4	4.3	11.4	1.33	54
3	4	2.2	22.0	1.37	56
4	6	6.5	10.7	1.27	62
5	6	4.3	15.8	1.30	61
6	6	2.2	30.9	1.36	64

^aAll polymerizations were carried out at 0 °C for 30 min in the presence of LiCl with [M]₀ = 0.05 mol/L and Ni(acac)₂/dppp ratio of 1/1.02. ^bEstimated by GPC with polystyrene as the standard and THF as eluent. ^cCalculated according to 4 or 6.

Table 4. Numbers of the Repeating Units in PF8 and P3HT Blocks (*m* and *n*, respectively), M_ns and PDIs of PF8-*b*-P3HT Diblock Copolymers FmTn

entry	polymer	<i>m</i> , <i>n</i> ^a	PF8 block		PF8- <i>b</i> -P3HT		yield ^c (%)
			M _n (kDa) ^b	PDI ^b	M _n (kDa) ^b	PDI ^b	
1	F21T37	21, 37	14.6	1.19	22.8	1.26	66
2	F19T71	19, 71	14.0	1.16	29.5	1.24	70
3	F34T34	34, 34	29.8	1.25	36.9	1.30	69
4	F35T74	35, 74	30.9	1.20	46.2	1.29	72

^aCalculated according to ¹H NMR spectra. ^bMeasured by GPC with polystyrene as the standard and THF as eluent. ^cOverall yield to the sum of 2 and 7 after Soxhlet extraction with acetone.

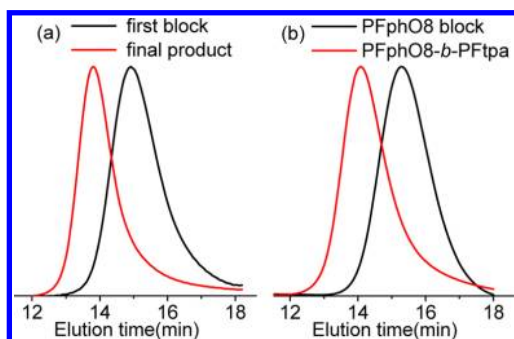


Figure 3. (a) GPC elution curves of PF8s obtained in “monomer addition” experiment (first block: M_n = 14.1 kDa, PDI = 1.20; final product: M_n = 28.5 kDa, PDI = 1.23). (b) GPC elution curves of PFphO8 block (M_n = 9.5 kDa, PDI = 1.25) and PFphO8-*b*-PFtpa (M_n = 18.2 kDa, PDI = 1.31).

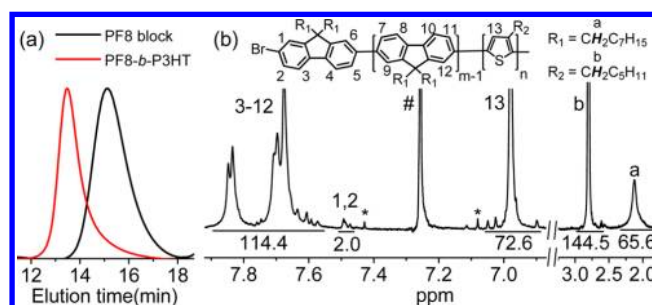
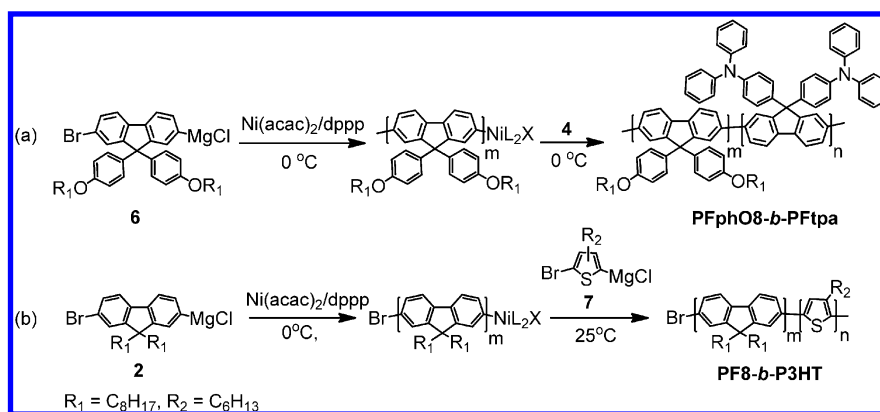


Figure 4. (a) GPC elution curves of PF8 block (M_n = 14.0 kDa, PDI = 1.16) and PF8-*b*-P3HT (F19T71, M_n = 29.5 kDa, PDI = 1.24). (b) ¹H NMR of spectrum (600 MHz, CDCl₃) of PF8-*b*-P3HT (F19T71, M_n = 29.5 kDa, PDI = 1.24). # and * are the signals of CHCl₃ and ¹³C satellites, respectively.

Scheme 3. Synthesis of Diblock Copolymers PFphO8-*b*-PFtpa (a) and PF8-*b*-P3HTs (b)

form a complex with an elongated-octahedral coordination geometry.³⁷ We found that the tetrahydrofuran (THF) solution of $\text{Ni}(\text{acac})_2/\text{dppp}$ also exhibited a diffuse and broad signal in ^{31}P NMR measurement, like the solution of $\text{Ni}(\text{acac})_2/\text{PMe}_2\text{Ph}_2$. So we surmise that $\text{Ni}(\text{acac})_2/\text{dppp}$ probably can in situ form similar complex and catalyze the KCTP of fluorene monomers. After several attempts, the single crystal of $\text{Ni}(\text{dppp})(\text{acac})_2$ were successfully obtained by diffusing hexane into toluene solution of $\text{Ni}(\text{acac})_2/\text{dppp}$. Figure 5 shows the

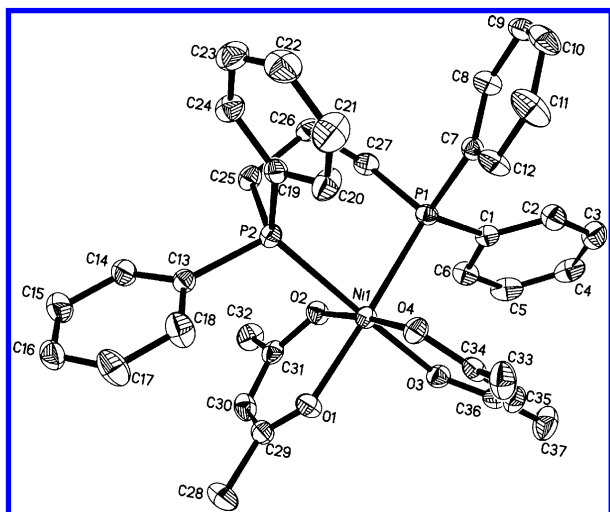


Figure 5. Molecular structure of $\text{Ni}(\text{dppp})(\text{acac})_2$. Thermal ellipsoids are drawn at the 30% probability level, and H atoms are omitted for clarity.

structure of $\text{Ni}(\text{dppp})(\text{acac})_2$ as determined by X-ray crystallographic analysis. The complex, which comprises one dppp and two acac, also displays an octahedral coordination geometry as the complex formed by $\text{Ni}(\text{acac})_2$ and PMe_2Ph . However, $\text{Ni}(\text{dppp})(\text{acac})_2$ exhibits slightly shorter Ni–O bond distances (2.034 and 2.016 Å, respectively) than complex trans- $[\text{Ni}(\text{acac})_2(\text{PMe}_2\text{Ph})_2]$ (2.045 and 2.028 Å, respectively), probably due to the steric effect of dppp. With this complex as the catalyst for the KCTP of **2**, PF8s with M_n s identical to those prepared with $\text{Ni}(\text{acac})_2/\text{dppp}$ were obtained (see Table 2 and 5). Above results imply that in situ formed $\text{Ni}(\text{acac})_2(\text{dppp})$ is probably the active catalyst in the polymerizations with $\text{Ni}(\text{acac})_2/\text{dppp}$ as the catalyst.

In order to understand the polymerization mechanism, the polymerization mixture of **2** with $\text{Ni}(\text{acac})_2/\text{dppp}$ as the catalyst was monitored with ^{31}P NMR spectrometer. For comparison, ^{31}P NMR spectrum of the polymerization mixture of **2** with $\text{Ni}(\text{dppp})\text{Cl}_2$ as the catalyst was also recorded. As

Table 5. Polymerization Results of **2 with Different Amounts of $\text{Ni}(\text{dppp})(\text{acac})_2$ as the Catalyst^a**

entry	$[\text{Ni}(\text{II})]/[\text{2}]_0$ (mol %)	M_n^b (kDa)	PDI ^b	yield ^c (%)
1	4.1	14.1	1.25	74
2	2.0	32.4	1.28	79
3	1.0	64.3	1.35	75

^aAll polymerizations were carried out at 0 °C for 30 min in the presence of 1 equiv LiCl with $[\text{2}]_0 = 0.05$ mol/L. $\text{Ni}(\text{dppp})(\text{acac})_2$ with additional 5 mol % dppp of the complex was used as the catalyst.

^bEstimated by GPC with polystyrene as the standard and THF as eluent. ^cCalculated according to 2.

shown in Figure S4, Supporting Information, the signals of the catalyst resting states are identical in these two polymerizations. On the other hand, according to the previous report,²⁸ significant amount of polymer chains are Br/Br ended when $\text{Ni}(\text{dppp})\text{Cl}_2$ is used as the catalyst. Two parallel polymerizations with 2.1 mol % $\text{Ni}(\text{dppp})\text{Cl}_2$ and $\text{Ni}(\text{acac})_2/\text{dppp}$ as the catalysts, respectively, were also conducted. Noticeable amount of oligomeric products (mainly dimer and trimer) were found in the polymerization mixture with $\text{Ni}(\text{dppp})\text{Cl}_2$ as the catalyst. In contrast, the GPC curve of the polymerization mixture with $\text{Ni}(\text{acac})_2/\text{dppp}$ as the catalyst only exhibited the peaks corresponding to the polymeric product and unreacted monomer (Figure S5, Supporting Information). From all above results, we speculate that acac may play an important role in the intramolecular catalyst transfer process, especially in the early stage of the polymerization.

CONCLUSION

Phosphine ligands have been screened for the KCTP of fluorene monomers with $\text{Ni}(\text{acac})_2/\text{phosphine}$ ligand as the catalyst. It was found that $\text{Ni}(\text{acac})_2/\text{dppp}$ is a promising catalyst system for the controlled polymerization of fluorene monomers. The M_n s of afforded PF8s were linear to the conversions of **2** with PDIs of 1.1–1.3 and could be controlled in the range of 2.8–62.2 kDa by tuning the amount of the catalyst, indicating a “living” nature of the polymerization. PFs with phenyl and triphenylamine substituents at 9-position of fluorene units were also synthesized in a controlled manner. The “living” characteristics of the polymerization were also confirmed by “monomer addition” experiment and block copolymerizations, and PF-based diblock copolymers, i.e., PFphO8-*b*-PFtpa and PF8-*b*-P3HT, with M_n up to 46 kDa could be easily synthesized. All these indicate that KCTP is a powerful protocol for the controlled synthesis of fluorene-based conjugated polymers while appropriate ligands are selected.

EXPERIMENTAL SECTION

Materials. THF was distilled over sodium-benzophenone. Isopropylmagnesium chloride (PrMgCl , 2.0 M solution in THF, Acros), *tert*-butylmagnesium chloride (BuMgCl , 1.7 M solution in THF, Acros), $\text{Ni}(\text{dppp})\text{Cl}_2$ (Pacific ChemSource, Inc., Zhengzhou, China, 98%), $\text{Ni}(\text{acac})_2$ (Aladdin Reagent Database Inc., Shanghai, China, 95%), PPh_3 (Sigma-Aldrich Co. LLC., ≥ 95%), dppe (Sigma-Aldrich Co. LLC., 97%) and dppf (J&K Scientific Ltd., 98%) were used as received without further purification. dppp (Pacific ChemSource, Inc., Zhengzhou, China, 98%) were recrystallized from alcohol. Lithium chloride (LiCl, Acros) was heated at 130 °C in vacuum for 5 h prior to use. 2-Bromo-7-iodo-9,9-dioctylfluorene (**1**),⁴² 2,5-dibromo-3-hexylthiophene,⁴³ 1,4-dihexyloxybenzene⁴⁴ and 1,4-dioctyloxybenzene⁴⁴ were synthesized according to the references. Their purities are all above 99.5% according to GC–MS measurements. The synthesis of 9,9-di(4-diphenylaminophenyl)-2-bromo-7-iodofluorene (**3**) and 9,9-di(4-*n*-octyloxyphenyl)-2-bromo-7-iodofluorene (**5**) is included in the Supporting Information (Scheme S1).

Instrumentation. ^1H NMR spectra were recorded on Bruker AV 600 spectrometer in CDCl_3 with tetramethylsilane (TMS) as the internal reference. GC–MS measurements were carried out on an Agilent 5975/6890N GC–MS instrument equipped with an Agilent HP-5 column (30 m). 1,4-Dihexyloxybenzene or 1,4-dioctyloxybenzene was used as the internal reference. GPC analysis was conducted on a Waters 2414 system equipped with Waters HT4 and HT3 column-assembly and a Waters 2414 refractive index detector (eluent, THF; flow rate, 1.00 mL/min; temperature, 40 °C; standard, polystyrene). MALDI–TOF mass spectra were recorded in a linear mode on a Kratos AXIMA-CFR Kompact MALDI Mass Spectrometer

with anthracene-1,8,9-triol as the matrix. Single crystal data collection was carried out with graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) on a Bruker Smart APEX diffractometer with a charge-coupled device (CCD) detector and graphite monochromator. Lorentz and polarization corrections were applied to the data sets. The intensity data were collected in ω scan mode. The crystal structure was solved using the SHELXTL program and refined using full matrix least-squares. The hydrogen atom positions were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbon atoms.

Preparation of Ni(acac)₂/Ligand Solutions. In a typical experiment (ligand = dppp, Ni(acac)₂/dppp = 1/1.02), 10 mL THF was added into a mixture of Ni(acac)₂ (51.4 mg, 0.20 mmol) and dppp (84.1 mg, 0.204 mmol) in a 25 mL Schlenk tube flushed with argon. Then the solution was stirred at 25 °C for 20 min and directly used the polymerization.

Synthesis of PF8 with Ni(acac)₂/dppp. In a typical experiment (1.1 mol % Ni(acac)₂/dppp as the catalyst, Table 2, entry 5), into a mixture of **1** (595.4 mg, 1.00 mmol), LiCl (42.4 mg, 1.00 mmol), 1,4-bis(hexyloxy)benzene (69.5 mg, 0.25 mmol) and THF (20 mL) in a 50 mL Schlenk tube was added a THF solution of ⁱPrMgCl (0.98 mmol) at −20 °C under argon. The mixture was stirred for 1 h (conversion of **1** was 93% as measured by GC–MS). Then, 0.5 mL Ni(acac)₂/dppp THF solution was added. After polymerizing at 0 °C for 30 min, the polymerization was quenched with HCl aqueous solution (5 M, 5 mL). The mixture was poured into water and extracted with toluene. The organic extracts were washed with brine and dried over MgSO₄ (conversion of **2** was 88% as measured by GC–MS). After the solvent was removed under reduced pressure, the GPC measurement was conducted ($M_n = 62.2$ kDa, PDI = 1.23). The polymer was further purified by the precipitation into methanol (291.0 mg, 80%). ¹H NMR (CDCl₃) δ (ppm) 7.78–7.90 (m, 2H), 7.76–7.58 (m, 4H), 2.12 (br, 4H), 1.28–1.01 (m, 20H), 0.78–0.91 (m, 10H).

Synthesis of PFtpa with Ni(acac)₂/dppp. In a typical experiment (6.5 mol % Ni(acac)₂/dppp as the catalyst, Table 3, entry 1), into a mixture of **3** (428.8 mg, 0.50 mmol), LiCl (21.2 mg, 0.50 mmol) and THF (10 mL) in a 25 mL Schlenk tube was added a THF solution of ⁱPrMgCl (0.49 mmol) at −20 °C under argon. The mixture was stirred for 1 h (conversion of **3** was 92% as measured by ¹H NMR). Then, 1.5 mL Ni(acac)₂/dppp THF solution was added. After polymerizing at 0 °C for 30 min, the polymerization was quenched with HCl aqueous solution (5 M, 5 mL). The mixture was poured into water and extracted with toluene. The organic extracts were washed with brine and dried over MgSO₄. After the solvent was removed under reduced pressure, the GPC measurement was conducted ($M_n = 8.8$ kDa, PDI = 1.28). The polymer was further purified by the precipitation into acetone (191.9 mg, 59%). ¹H NMR (CDCl₃) δ (ppm) 7.82–7.71 (br, 2H), 7.64–7.48 (br, 4H), 7.18–6.85 (m, 28H).

Synthesis of PFphO8 with Ni(acac)₂/dppp. In a typical experiment (6.5 mol % Ni(acac)₂/dppp as the catalyst, Table 3, entry 4), into a mixture of **5** (389.8 mg, 0.50 mmol), LiCl (21.2 mg, 0.50 mmol) and THF (10 mL) in a 25 mL Schlenk tube was added a THF solution of ⁱPrMgCl (0.49 mmol) at −20 °C under argon. The mixture was stirred for 1 h (conversion of **5** was 92% as measured by ¹H NMR). Then, 1.5 mL Ni(acac)₂/dppp THF solution was added. After polymerizing at 0 °C for 30 min, the polymerization was quenched with HCl aqueous solution (5 M, 5 mL). The mixture was poured into water and extracted with toluene. The organic extracts were washed with brine and dried over MgSO₄. After the solvent was removed under reduced pressure, the GPC measurement was conducted ($M_n = 10.7$ kDa, PDI = 1.27). The polymer was further purified by the precipitation into acetone (177.5 mg, 62%). ¹H NMR (CDCl₃) δ (ppm) 7.76–7.73 (br, 2H), 7.55–7.47 (br, 4H), 7.16 (d, $J = 8$ Hz, 4H), 6.75 (d, $J = 9$ Hz, 4H), 3.88 (br, 4H), 1.73 (br, 4H), 1.41 (br, 4H), 1.36 (br, 16H), 0.86 (br, 6H).

Polymerization Kinetic Experiments. In a typical experiment (2.1 mol % Ni(acac)₂/dppp as the catalyst), into a mixture of **1** (595.4 mg, 1.00 mmol), LiCl (42.4 mg, 1.00 mmol), 1,4-bis(hexyloxy)benzene (69.5 mg, 0.25 mmol) and THF (20 mL) in a 50 mL Schlenk tube was added a THF solution of ⁱPrMgCl (0.98 mmol) at −20 °C

under argon. The mixture was stirred for 1 h (conversion of **1** was 95% as measured by GC–MS). Then, the mixture was warmed to 0 °C. After addition of Ni(acac)₂/dppp THF solution (1.0 mL), aliquots (2 mL) were taken at different time intervals. Each aliquot was quenched with HCl aqueous solution (5 M, 1 mL), poured into water and extracted with toluene. The organic extracts were washed with brine and dried over MgSO₄ for GC–MS measurements (conversions of **2** were measured by GC–MS, respectively). After the solvents were removed under reduced pressure, the GPC measurement was conducted.

“Monomer Addition” Experiment. Into a mixture of **1** (297.7 mg, 0.50 mmol), LiCl (21.2 mg, 0.50 mmol), 1,4-bis(hexyloxy)benzene (34.8 mg, 0.125 mmol) and THF (10 mL) in a 25 mL Schlenk tube (A) was added a THF solution of ⁱPrMgCl (0.49 mmol) at −20 °C under argon. The mixture was stirred for 1 h. Then, 5 mL mixture solution was taken out and added to another dry 25 mL Schlenk tube (B) flushed with argon. After addition of Ni(acac)₂/dppp THF solution (0.5 mL) to the tube (B), the polymerization was carried out at 0 °C for 4 min, and 0.2 mL solution was taken out and quenched with HCl aqueous solution (5 M, 1 mL). The residual mixture solution in tube A was also added to tube B. After further polymerizing for 6 min, the polymerization was quenched with HCl aqueous solution (5 M, 4 mL). The polymerization mixtures were poured into water and extracted with toluene. The organic extracts were washed with brine and dried over MgSO₄. After the solvents were removed under reduced pressure, the GPC measurements were conducted (the first block, $M_n = 14.1$ kDa, PDI = 1.20; the final product, $M_n = 28.5$ kDa, PDI = 1.23).

Synthesis of PFphO8-*b*-PFtpa with Ni(acac)₂/dppp. Into a mixture of **3** (214.4 mg, 0.25 mmol), LiCl (10.6 mg, 0.25 mmol) and THF (5 mL) in a 25 mL Schlenk tube (A) was added a THF solution of ⁱPrMgCl (0.245 mmol) at −20 °C under argon. The mixture was stirred for 1 h (conversion of **3** was 91% as measured by ¹H NMR). Into a mixture of **5** (194.9 mg, 0.25 mmol), LiCl (10.6 mg, 0.25 mmol) and THF (5 mL) in a 25 mL Schlenk tube (B) was added a THF solution of ⁱPrMgCl (0.245 mmol) at −20 °C under argon. The mixture was stirred for 1 h (conversion of **5** was 90% as measured by ¹H NMR). Then, 0.75 mL Ni(acac)₂/dppp THF solution was added to tube B. After polymerizing at 0 °C for 5 min, 1.2 mL solution was withdrawn and quenched with HCl aqueous solution (5 M, 2 mL). Then 4 mL mixture solution in tube A was added to tube B, and the reaction temperature was kept at 0 °C for 30 min before the polymerization was quenched with HCl aqueous solution (5 M, 5 mL). The polymerization mixtures were respectively poured into water and extracted with toluene. The organic extracts were washed with brine and dried over MgSO₄. After the solvents were removed under reduced pressure, the GPC measurement was conducted (PFphO8 block, $M_n = 9.5$ kDa, PDI = 1.25; PFphO8-*b*-PFtpa, $M_n = 18.2$ kDa, PDI = 1.31). The PFphO8-*b*-PFtpa was further purified by the precipitation from toluene solution into acetone (157.8 mg, 65%).

Synthesis of PF8-*b*-P3HT with Ni(acac)₂/dppp. In a typical experiment (F19T71, Table 2, entry 2), into a mixture of 2,5-dibromo-3-hexylthiophene (521.7 mg, 1.60 mmol), LiCl (67.8 mg, 1.60 mmol), 1,4-dioctyloxybenzene (200.7 mg, 0.60 mmol) and THF (16 mL) in a 50 mL Schlenk tube (A) was added a THF solution of ⁱBuMgCl (1.57 mmol) at 25 °C under argon. The mixture was stirred for 24 h (conversion of 2,5-dibromo-3-hexylthiophene was 91% as measured by GC–MS). Into a mixture of **1** (297.7 mg, 0.50 mmol), LiCl (21.2 mg, 0.50 mmol), 1,4-bis(hexyloxy)benzene (55.7 mg, 0.20 mmol) and THF (10 mL) in a 25 mL Schlenk tube (B) was added a THF solution of ⁱPrMgCl (0.49 mmol) at −20 °C under argon. The mixture was stirred for 1 h (conversion of **1** was 94% as measured by GC–MS). Then, 1 mL Ni(acac)₂/dppp THF solution was added to tube B. After polymerizing at 0 °C for 4 min, 2.2 mL solution was withdrawn and quenched with HCl aqueous solution (5 M, 2 mL). Then all of the mixture solution in tube A was added to tube B, and the reaction temperature was allowed to rise to 25 °C. After polymerizing for 30 min, the polymerization was quenched with HCl aqueous solution (5 M, 10 mL). The polymerization mixtures were respectively poured into water and extracted with toluene. The organic extracts were

washed with brine and dried over MgSO_4 (conversions of **2** was 82% and conversions of **3** was 75% as measured by GC–MS). After the solvents were removed under reduced pressure, the GPC measurement were conducted (PF8 block, $M_n = 14.0$ kDa, PDI = 1.16; PF8-*b*-P3HT, $M_n = 29.5$ kDa, PDI = 1.24). The PF8-*b*-P3HT was further purified by the precipitation into methanol then Soxhlet extraction with acetone (271.5 mg, 73%).

Synthesis of the Complex $\text{Ni}(\text{dppp})(\text{acac})_2$. Into a mixture of $\text{Ni}(\text{acac})_2$ (128.5 mg, 0.5 mmol) and dppp (210.3 mg, 0.51 mmol) in a 50 mL vial was added 20 mL of THF under argon. The light-blue solution was stirred at -30°C for 12 h and concentrated in vacuo until ~ 2 mL of solution was left. Hexane (30 mL) was added and the resulting solid was filtered and washed with additional 30 mL hexane. The crude product was purified by recrystallization in toluene/hexane at -20°C to afford the complex as blue crystals in a yield of 65% (136.7 mg). The single crystals of $\text{Ni}(\text{dppp})(\text{acac})_2$ were prepared by slowly diffusing hexane into its toluene solution at -20°C .

Synthesis of PF8 with $\text{Ni}(\text{dppp})(\text{acac})_2$. In a typical experiment (4.1 mol % $\text{Ni}(\text{acac})_2(\text{dppp})$ as the catalyst, Table S, entry 1), into a mixture of **1** (595.4 mg, 1.00 mmol), LiCl (42.4 mg, 1.00 mmol), 1,4-bis(hexyloxy)benzene (69.5 mg, 0.25 mmol) and THF (20 mL) in a 50 mL Schlenk tube (A) was added a THF solution of $^i\text{PrMgCl}$ (0.98 mmol) at -20°C under argon. The mixture was stirred for 1 h (conversion of **1** was 97% as measured by GC–MS). At the same time, 2 mL of THF was added into a mixture of $\text{Ni}(\text{acac})_2(\text{dppp})$ (26.8 mg, 0.04 mmol) and dppp (0.8 mg, 0.002 mmol) in a 10 mL Schlenk tube (B) flushed with argon to give a homogeneous blue solution. Then, this solution was added to Schlenk tube A. After polymerizing at 0°C for 30 min, the polymerization was quenched with HCl aqueous solution (5 M, 5 mL). The mixture was poured into water and extracted with toluene. The organic extracts were washed with brine and dried over MgSO_4 (conversion of **2** was 86% as measured by GC–MS). After the solvent was removed under reduced pressure, the GPC measurement was conducted ($M_n = 14.1$ kDa, PDI = 1.25). The polymer was further purified by the precipitation into methanol (285.6 mg, 74%).

■ ASSOCIATED CONTENT

■ Supporting Information

Synthesis procedures of the compounds **3** and **5**, crystallographic data for the complex $\text{Ni}(\text{dppp})(\text{acac})_2$, the calibration curve of PF8s, GPC elution curves and ^1H NMR spectra of PF8-*b*-P3HTs, GPC elution curves of PF8s with 2.1 mol % $\text{Ni}(\text{dppp})\text{Cl}_2$ or $\text{Ni}(\text{acac})_2/\text{dppp}$ as the catalyst, and ^{31}P NMR spectra of the polymerization mixtures of **2** with 10 mol % $\text{Ni}(\text{dppp})\text{Cl}_2$ or $\text{Ni}(\text{acac})_2/\text{dppp}$ as the catalyst. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yhgeng@ciac.jl.cn.

Present Address

[§]Corporate R&D, 3M China, Shanghai 200233, P. R. China.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by National Basic Research Program of China (973 Project, No. 2009CB623603) of Chinese Ministry of Science and Technology, and NSFC (Nos. 20921061, 20923003 and 21074131).

■ REFERENCES

- (1) Facchetti, A. *Chem. Mater.* **2011**, *23*, 733.
- (2) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. E.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897.
- (3) Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010**, *110*, 3.
- (4) Yamamoto, T. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 431.
- (5) Fréchet, J. M.; Beaujuge, P. M. *J. Am. Chem. Soc.* **2011**, *133*, 20009.
- (6) Coffin, R. C.; Peet, J.; Rogers, J.; Bazan, G. C. *Nature Chem.* **2009**, *1*, 657.
- (7) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365.
- (8) Park, J. K.; Jo, J.; Seo, J. H.; Moon, J. S.; Park, Y. D.; Lee, K.; Heeger, A. J.; Bazan, G. C. *Adv. Mater.* **2011**, *23*, 2430.
- (9) Scherf, U.; Gutacker, A.; Koenen, N. *Acc. Chem. Res.* **2008**, *41*, 1086.
- (10) Kiriy, A.; Senkovskyy, V.; Sommer, M. *Macromol. Rapid Commun.* **2011**, *32*, 1503.
- (11) Okamoto, K.; Luscombe, C. K. *Polym. Chem.* **2011**, *2*, 2424.
- (12) Geng, Y. H.; Huang, L.; Wu, S. P.; Wang, F. S. *Sci. China Ser. B: Chem.* **2010**, *53*, 1620.
- (13) Yokozawa, T.; Yokoyama, A. *Chem. Rev.* **2009**, *109*, 5595.
- (14) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169.
- (15) Sheina, E. E.; Liu, J. S.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526.
- (16) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542.
- (17) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromol. Rapid Commun.* **2004**, *25*, 1663.
- (18) Vallat, P.; Lamps, J. -P.; Schosseler, F.; Rawiso, M.; Catala, J.-M. *Macromolecules* **2007**, *40*, 2600.
- (19) Yokozawa, T.; Adachi, I.; Miyakoshi, R.; Yokoyama, A. *High Perform. Polymers* **2007**, *19*, 684.
- (20) Senkovskyy, V.; Tkachov, R.; Beryozkina, T.; Komber, H.; Oertel, H.; Horecha, M.; Bocharova, V.; Stamm, M.; Gevorgyan, S. A.; Krebs, F. C.; Kiriy, A. *J. Am. Chem. Soc.* **2009**, *131*, 16445.
- (21) Smeets, A.; Van den Bergh, K.; Winter, J. D.; Gerbaux, P.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2009**, *42*, 7638.
- (22) Bronstein, H. A.; Luscombe, C. K. *J. Am. Chem. Soc.* **2009**, *131*, 12894.
- (23) Locke, J. R.; McNeil, A. J. *Macromolecules* **2010**, *43*, 8709.
- (24) Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2006**, *128*, 16012.
- (25) Yokoyama, A.; Kato, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2008**, *41*, 7271.
- (26) Nanashima, Y.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2012**, *45*, 2609.
- (27) Wu, S.; Sun, Y.; Huang, L.; Wang, J.; Zhou, Y.; Geng, Y.; Wang, F. *Macromolecules* **2010**, *43*, 4438.
- (28) Huang, L.; Wu, S. P.; Qu, Y.; Geng, Y. H.; Wang, F. S. *Macromolecules* **2008**, *41*, 8944.
- (29) Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D. *Macromolecules* **2009**, *42*, 30.
- (30) Javier, A. E.; Varshney, S. R.; McCullough, R. D. *Macromolecules* **2010**, *43*, 3233.
- (31) Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A. *Macromolecules* **2008**, *41*, 7817.
- (32) Bryan, Z. J.; Smith, M. L.; McNeil, A. J. *Macromol. Rapid Commun.* **2012**, DOI: 10.1002/marc.201200096.
- (33) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236.
- (34) Yokozawa, T.; Kohno, H.; Ohta, Y.; Yokoyama, A. *Macromolecules* **2010**, *43*, 7095.
- (35) Lanni, E. L.; Locke, J. R.; Gleave, C. M.; McNeil, A. J. *Macromolecules* **2011**, *44*, 5136.
- (36) Lee, S. R.; Bryan, Z. J.; Wagner, A. M.; McNeil, A. J. *Chem. Sci.* **2012**, *3*, 1562.
- (37) Ananikov, V. P.; Gayduk, K. A.; Starikova, Z. A.; Beletskaya, I. P. *Organometallics* **2010**, *29*, 5098.
- (38) Wang, Q. L.; Qu, Y.; Tian, H. K.; Geng, Y. H.; Wang, F. S. *Macromolecules* **2011**, *44*, 1256.

- (39) Geng, Y. H.; Trajkovska, A.; Katsis, D.; Ou, J. J.; Culligan, S. W.; Chen, S. H. *J. Am. Chem. Soc.* **2002**, *124*, 8337.
- (40) Chen, S. A.; Lu, H. H.; Huang, C. W. *Adv. Polym. Sci.* **2008**, *212*, 49.
- (41) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365.
- (42) Maji, M. S.; Pfeifer, T.; Studer, A. *Chem.—Eur. J.* **2010**, *16*, 5872.
- (43) Loewe, R. S.; Ewbank, P. C.; Liu, J. S.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324.
- (44) Plater, M. J.; Sinclair, J. P.; Aiken, S.; Gelbrich, T.; Hursthouse, M. B. *Tetrahedron* **2004**, *60*, 6385.