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Kumada chain-growth polycondensation as a universal method for synthesis of well-defined conjugated polymers

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Kumada chain-growth polycondensation (KCGP) is a novel method for the synthesis of well-defined conjugated polymers. Because the Ni-catalyst can transfer in an intramolecular process to the propagating chain end, the polymerization follows chain-growth mechanism. With this newly developed method, various conjugated polymers, such as polythiophenes, poly(*p*-phenylene) (PPP), polypyrrole (PPy), and polyfluorene with controlled molecular weights and relatively narrow polydispersities (PDIs), have been prepared. Especially, the polymerizations for poly(3-alkylthiophene)s (P3ATs), PPP, and PPy exhibited quasi-living characteristics, which allows preparing polymer brushes, fully-conjugated block copolymers, and macroinitiators and macro-reactants for the synthesis of rod-coil block copolymers. In the current review, the progress in this new area is summarized.

chain growth polycondensation, conjugated polymers, Kumada reaction, block copolymers, polymer brush

1 Introduction

In the past twenty years, conjugated polymers have attracted increasing attention due to their applications in polymer light-emitting diodes (PLEDs) [1], polymer solar cells (PSCs) [2], organic thin film transistors (OTFTs) [3] and chemical sensors [4]. Chain structures of the conjugated polymers not only determine the energy levels at the molecular level, but also play a significant role in controlling the intermolecular interaction and morphology in the solid state for tuning properties, such as absorption, photoluminescence, charge carrier injection/transport, energy transfer and charge separation. Chain-ends, chain defects and impurities all have critical impact on overall properties of the conjugated polymers. For instance, polyfluorenes containing orange or green/red dopants, which are appropriately connected to the polymer chain, can be used for the fabrication of highly efficient white PLEDs [5, 6]. Regioregularity of poly(3-alkylthiophene)s (P3ATs) has pronounced effect on their self-assembly structure and therefore properties [7], and regioregular poly(3-hexylthiophene) (P3HT) forms highly ordered films for high performance OTFTs [8]. Moreover, it was found that the films of P3HT comprised densely packed nanofibrils with the width related to polymer chain length, and a distinct correlation between OTFT mobility, molecular weight and nanostructures has been established [9]. Conjugated block copolymers/cooligomers form phase-separated nanostructures to afford efficient charge separation and transport for PSCs [10, 11]. Catalyst residues, chain-ends (such as bromine and boronic acid) could quench the electroluminescence and significantly reduce the life-time of the optoelectronic devices [12]. All these suggest that high purity conjugated polymers with well-defined structures are essential for high performance optoelectronic devices. Accordingly, development of well-

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*Corresponding author (email: yhgeng@ciac.jl.cn) controlled polymerizations is very significant.

Most of the conjugated polymers are synthesized by transition metal complex (typically Ni and Pd-complexes) catalyzed coupling reactions, such as Suzuki, Yamamoto, Stille, Heck, Kumada and Sonogashira couplings. The catalytic cycle of these reactions usually involves three steps: oxidative addition, transmetalation and reductive elimination [13]. Consequently, the polymerizations usually follow the step-growth mechanism, and require high purity monomers and long reaction time to achieve a high molecular weight. However, the molecular weight, polydispersity (PDI = M_n/M_w, M_n = number average molecular weight; M_w = weight average molecular weight) and chain-ends of the resulting polymers from step-growth polymerizations are in general poorly controlled. In comparison, chain-growth polymerizations are better controlled in terms of these parameters. Particularly, block copolymers could be prepared via chain-growth polymerizations with "living" nature.

In 2004, Yokozawa *et al.* found that Ni(dppp)Cl_2 (dppp = 1,3-bis(diphenyl phosphino)propane) catalyzed Kumada polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene followed chain-growth mechanism [14]. Since then, this new polymerization method, which is named Kumada chain growth polycondensation (KCGP) by us, evolves very fast under the effort of researchers all over the world. Conjugated polymers with diversity of architectures, such as conjugated homopolymers, rod-rod and rod-coil block copolymers, and functional polymer brushes, have been prepared. Although some accomplishments have been outlined in Yokozawa's reviews on various chain-growth polycondensations [15–17], it still lacks an article to specially introduce KCGP. In the current review, we hope to give a comprehensive overview on this topic. Although intramolecular catalyst transfer was also found in Suzuki coupling for preparing well-defined conjugated polymers via chain-growth polycondensation and hyper-branched polymers with a degree of branching of 100% [18–20], we will not include these works in the current review.

2 Kumada cross-coupling reaction

Ni- or Pd-catalyzed cross coupling reaction of Grignard reagents with alkyl, vinyl or aryl halides is named Kumada cross-coupling, which was first reported in 1972 by Kumada [21]. Grignard reagents are easily accessible through metal-halogen exchange reactions [22]. Particularly, development of lithium salts (such as LiCl) mediated Mg/Br or I exchange makes the preparation of versatile functional Grignard reagents possible [23, 24]. All these allow Kumada cross-coupling to be a powerful protocol for the preparation of new aromatic derivatives and conjugated oligomers and polymers.

Like other transition metal-catalyzed cross-coupling reactions, Kumada cross coupling also involves three consecutive steps in a catalytic cycle, which are oxidative addition, transmetalation and reductive elimination as shown in Figure 1. Typically, Pd(II) and Ni(II) complexes are used as the catalyst, and Pd(0) and Ni(0) are produced *in-situ* by reduction with 2 equiv of Grignard reagent.

From the catalytic cycle (Figure 1), the polymerization for conjugated polymers based on Kumada cross coupling should only be able to proceed in the step-growth mechanism. However, some clues in the references, whose significance was not realized before, are probably crucial to the success of KCGP. (1) Ligand exchange is probably the first irreversible step in the Ni-catalyzed Kumada cross coupling, and then the Ni catalyst undergoes oxidative addition immediately after the formation of Ni/haloarene π-complex (Figure 2) [25]. (2) "Ring-walking" of Ni(0) to the vinylarenes terminal for oxidative addition to aryl-Br or aryl-I bond as shown in Figure 3 was found to be a quantitative process under mild reaction conditions. Accordingly, it is expected that Ni(0) from reductive elimination could also form Ni/haloarene π-complex with products instead of diffusing into the reaction solution for the next catalytic cycle [26].

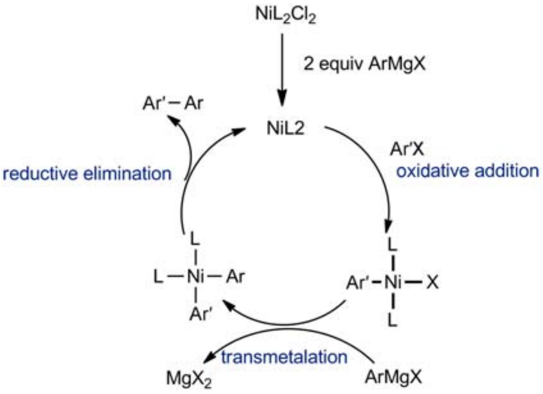


Figure 1 Catalytic cycle of Kumada cross-coupling.

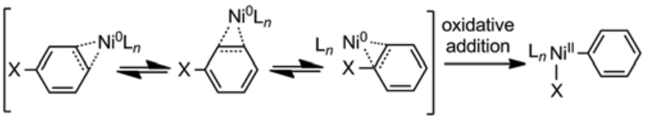


Figure 2 Complexation of the Ni(0) on the π-face of phenyl followed by the oxidative addition process [25].

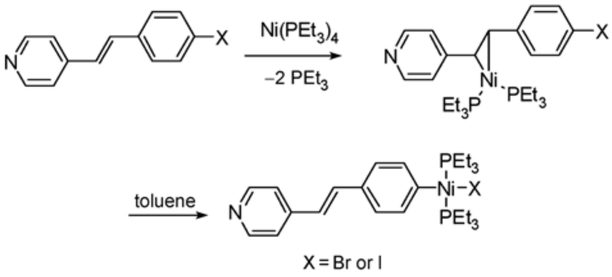


Figure 3 Selective η^2-(C=C) coordination of Ni(PEt_3)$_4$ followed by activation of the aryl-halide bond [26].

If an aryl-halogen bond is in the neighboring position, consecutive oxidative addition will take place through a "ring-walking" process. Actually, results from the cross-coupling of small molecular substances also support this speculation. When thienylmagnesium bromide reacts with 2,5-dibromothiophene in the presence of Ni-catalyst, 2,2′; 5,2″-terthiophene is always the dominant product even if 2,5-dibromothiophene is excess.

3 Polythiophenes and polymerization mechanism

Polymerization for regioregular P3ATs based on Kumada cross coupling was first developed in the early 1990s of the last century by McCullough *et al.* [27, 28], and the regioregular P3HT remains a state-of-the-art semiconducting polymer for OTFTs and PSCs [2, 3]. However, it is believed that the polymerization follows the step-growth mechanism for over 10 years until Yokozawa *et al.* found that the polymerization followed chain-growth mechanism in 2004 [14]. As shown in Figure 4(a), addition of Ni(dppp)Cl_2 into the THF solution of the Grignard reagent **2** and stirring at room temperature afforded regioregular P3HT. M_n-Conversion was linear in the polymerization process. M_n also increased linearly in proportion to the feed ratio of $[\mathbf{2}]_0$ and the catalyst. Meanwhile, PDI was $\leqslant 1.4$. All these results indicate that the polymerization followed the chain-growth mechanism with "living" polymerization characteristics. The chain- growth nature was also confirmed by "monomer-addition" experiments. When the second portion of monomer **2** was added into the polymerization mixture, the gel permeation chromatography (GPC) profile of the polymer shifted toward the high molecular region with narrow PDI remained. However, there was always a shoulder peak in the GPC profile at high molecular region with a M_n about twice of that corresponding to the main peak. Later, they found that this shoulder originated from the disproportionation of the active chain (P3HT-Ni(II)-Br) in the workup process. This side-reaction can be avoided by quenching the polymerization mixture with 5 M hydrochloride acid, and P3HT with M_n of 28700 and PDI as low as 1.14 were obtained [29]. Through similar experiments, McCullough *et al.* also confirmed this polymerization mechanism with 2,5-dibromo- 3-hexylthiophene as the starting material (Figure 4(b)) [30, 31]. Although the metal-halogen exchange product is a mixture of **2** and **2′** with a ratio of ~85:15, the polymerization still affords regioregular P3ATs because **2′** does not participate the polymerization mainly due to the steric effect [32, 33]. Geng *et al.* found that the polymerization of **2** with Ni(dppe)Cl_2 (dppe = 1,2-bis(diphenyl phosphino)ethane) as the catalyst in the presence of LiCl also proceeded in the chain-growth manner [34].

In order to unravel and understand this new polymerization, several groups have done tremendous research on the polymerization mechanism for P3HT. Yokozawa *et al.* first systematically studied the polymer chain ends, propagating group and initiator for Ni(dppp)Cl_2 catalyzed polymerization for P3HT [35]. Based on matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometric analysis, they found that all the polymers had Br/H chain ends. That means the polymer chains have bromine at one end and proton at the other end. Therefore, only one single kind of propagating group is involved in the polymerization. Because H-end can be produced by quenching both magnesiochloride end groups and Ni complex groups (P3HT-Ni(II)-Br), it is hard to identify the propagating group to confirm the chain-growth mechanism only from this evidence. They did the end-capping after polymerization with 3,4-dimethylphenylmagnesium chloride and again characterized the chain end structure by means of MALDI-TOF mass spectrometry. Only one series of peaks, the values of which corresponded to P3HT with $Me_2C_6H_3/Me_2C_6H_3$ end groups, were found in the spectrum. This indicates that the propagating species carry Br/Ni complex ends. Meanwhile, the average degree of polymerization (DP_n) and M_n of the end-capped P3HT were determined by ^{1}H NMR. The resulting DP_n was consistent with the feed ratio of the converted monomer to the Ni catalyst, indicating that one catalyst molecule formed one polymer chain. Combining all these data, they proposed the chain-growth mechanism. As shown in Figure 5, 2 equiv of **2** react with Ni(dppp)Cl_2 to yield the Ni(0) **3**, which is immediately inserted into one C–Br bond of the bithiophene having two bromine atoms. Thus, the polymerization is initiated by **4**, and propagated by the coupling reaction between the polymer end group and monomer **2**, followed by the intramolecular transfer of the Ni(0) to the terminal C–Br bond to yield the polymer with Br/H ends after hydrolysis of the propagating Ni(II) complex. The mechanism proposed by McCullough *et al.* is similar, but they proposed that the "associate pair" (Figure 5) was formed by coordination of Ni(dppp) to the thiophene ring in a η^2- or η^4-bonded fashion [30, 31]. Because of the formation of this "associate pair", the next oxidative addition is dominated by an intramolecular process. McCullough

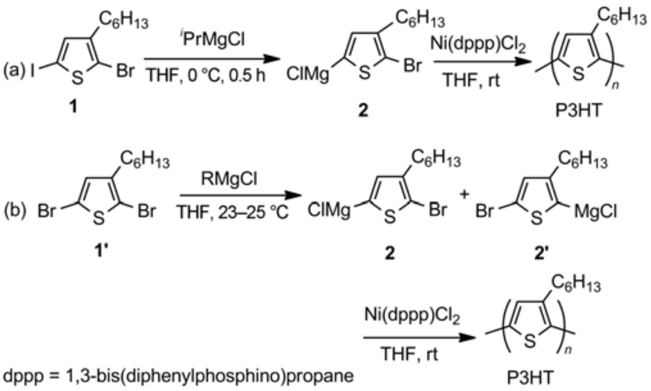


Figure 4 Yokozawa's (a) and McCullough's (b) routes for the synthesis of regioregular P3HT.

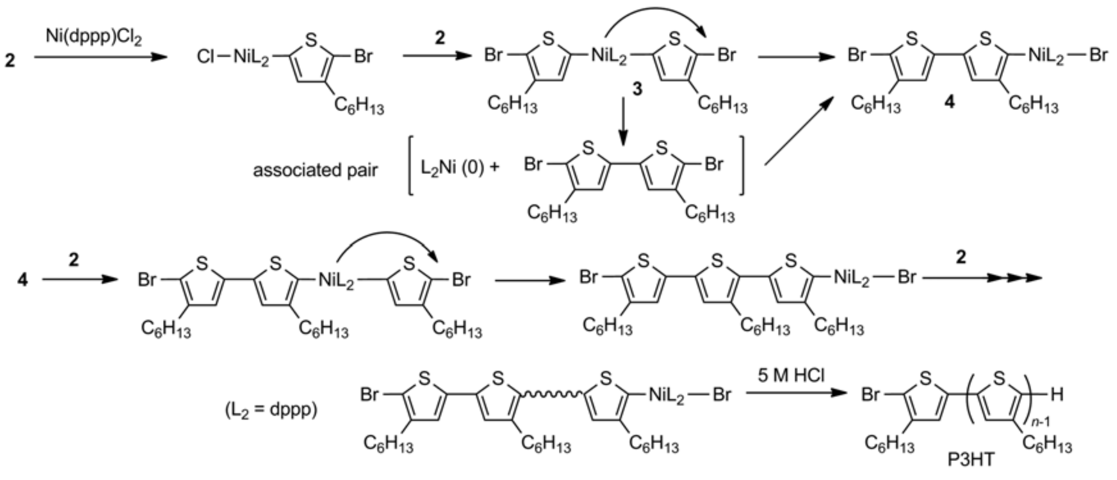


Figure 5 Proposed Kumada chain-growth polycondensation (KCGP) mechanism of P3HT.

et al. also carried out the end-capping experiments of P3HT using different Grignard reagents and studied the effect of the structure of the Grignard reagent on the end-capping efficiency. Capping with aryl Grignard reagents yielded the polymers with both ends capped. Because C=C and $C\equiv C$ groups can coordinate with the Ni-complex, allyl, ethynyl and vinyl Grignard reagents mainly afforded one-end capped P3HT [36]. This implies that Ni-complex rests on the chain terminus, and strongly supports the proposed propagation mechanism, i.e., Ni-complex moves to the chain end via intramolecular catalyst transfer for transmetalation with Grignard reagents

For chain growth polymerization without chain-transfer/termination, one initiator produces only one polymer chain. If this is exclusively demonstrated, the chain-growth nature of Kumada polymerization for P3HT will be unambiguous. Although Yokozawa *et al* [35]. demonstrated it is true by end-capping and MALDI-TOF mass spectrum, more evidence is necessary. According to Yokozawa's study, *in-situ* produced Ni-complex **4** served as the initiator. Kiriy first reported the polymerization of **2** with $(PPh_3)_2Ni(Ph)Br$ as the initiator [37]. However, only about ~80% P3HT was terminated by the Ph group from one side and by either hydrogen or bromine atoms at the opposite terminus (67% of Ph/H and 13% of Ph/Br P3HT). Moreover, ~20% H/H-terminated P3HT was also found. These indicate the presence of salient chain-transfer or termination, and $(PPh_3)_2Ni(Ph)Br$ is not as good as $Ni(dppp)Cl_2$ for controlling the polymerization. Luscombe *et al.* synthesized various catalysts, $(PPh_3)_2Ni(Aryl)Br$, and systematically studied the effect of the structure of the aryl group on the polymerization [38, 39]. Significant chain transfer/termination was observed, and therefore the polymerization did not show living characteristics. Finally, they made catalysts **5a** and **5b** with dppp as the phosphine ligand (Figure 6), and used these *in-situ* prepared catalysts for polymerization of **2** [40]. In the case of **5a**, ~5% impurity, which was believed to be $Ni(dppp)_2$, was observed. By contrast, clean **5b** could be prepared. With **5a** as the catalyst, a small amount of Ph/Br and H/H terminated P3HT was observed. While with **5b** as the catalyst, they prepared fully regioregular P3HT only with Tol/H terminus. The polymerization proceeded with living characteristics, as that catalyzed with $Ni(dppp)Cl_2$. These results strongly support the polymerization mechanism proposed by Yokozawa and McCullough.

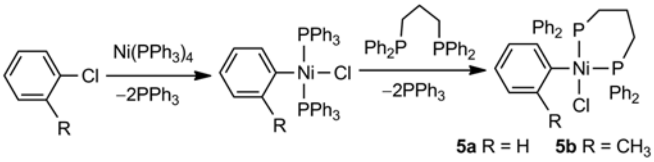


Figure 6 Route for preparation of external initiators.

According to the mechanism shown in Figure 5, chain propagation for P3HT involves three basic processes, i.e., intramolecular oxidative addition, transmetalation, and reductive elimination. These processes accordingly afford three complexes (**I**, **II** and **III**) as shown in Figure 7. Finding out which complex can be detected in the polymerization mixture is helpful for understanding the polymerization mechanism and further optimizing the polymerization condition. McCullough *et al.* first analyzed the polymerization rate of **2** with $Ni(dppp)Cl_2$ as the catalyst, and found the polymerization was first-order in both the monomer and the catalyst, suggesting that transmetalation is the rate-determining step [31]. McNeil *et al.* investigated the polymerization of **2** with $Ni(dppe)Cl_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) as the catalyst [41]. They found that the polymerization exhibited a first-order dependence on the catalyst concentration but a zeroth-order dependence on the monomer concentration. Moreover, they detected the reactive organometallic intermediates during and after the polymerization by means of ^{31}P NMR spectrometer, and found complexes **III** and **II** as the dominant intermediates during and

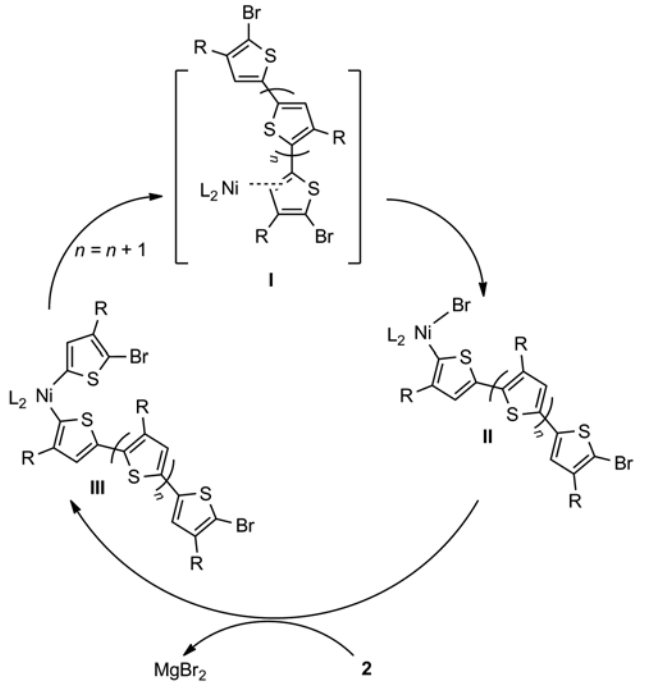


Figure 7 Possible complexes present in the polymerization for P3HT.

after the polymerization, respectively. These results indicate that the conversion of complex **I** to complex **II** and then **III** is fast and the rate-determining step is the reductive elimination. The difference between the polymerizations catalyzed by Ni(dppp)Cl_2 and Ni(dppe)Cl_2 suggests that the ligand has a strong influence on the rate-determining step. The presence of these intermediates is consistent with the "living" nature of the polymerization.

Regioregular polythiophenes with various substituents at the 3-position of thiophene have been prepared by KCGP (Figure 8). Encouraged by the preparation of P3HT, Yokozawa *et al.* studied the polymerization of the thienyl monomer carrying a [2-(2-methoxyethoxy)ethoxyl]methyl group at the 3-position (**PT1**) [42]. They found that the polymerization also followed chain growth mechanism. With Ni(dppe)Cl_2 as the catalyst at 0 °C, the polymer with low PDI and controlled molecular weight could be obtained. Br/Br and H/H end polymers were both observed in MALDI-TOF spectra, especially at high conversion of the monomer. They attributed this phenomenon to the presence of chain transfer. Catala *et al.* studied the polymerization of a thienyl monomer containing an ester group in the substituent (**PT2**) [43]. The thienyl Grignard reagent could be prepared by metal-halogen exchange at 0 °C, and the reaction of the ester group and Grignard reagent was not found. Although the Grignard monomer is not stable at room temperature, a polymer with M_n more than 20000 was prepared but with relatively large PDI. In the polymerization for **PT3**, LiCl has to be added to obtain the polymer with relatively narrow PDI. Moreover, the regio-selectivity was poor and only a regiorandom polymer was obtained [44]. Polymers **PT4**-**PT9** were also synthesized [45–50]. Although no detailed study on the polymerization mechanism was reported, the polymerization may also follow chain-growth mechanism. The polymerization for **PT5** has to be carried out at 70 °C [46]. At low temperature such as room temperature used in the preparation of P3HT, very little of the targeted polymer was obtained. This phenomenon is not surprising because the ethynyl group could capture the catalyst according to McCullough's report about the end-capping of P3HT [36].

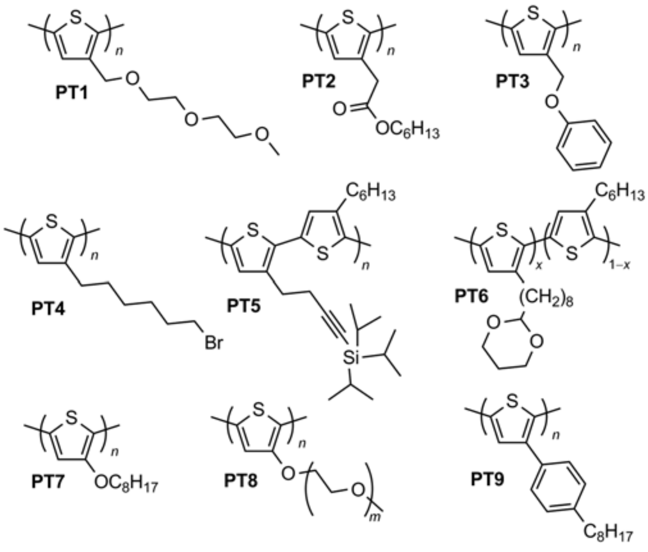


Figure 8 Structures of polythiophenes with different groups at position 3.

4 Other conjugated polymers

To evaluate whether KCGP is universal for conjugated polymers with a diversity of structures, the polymerizations of several aromatic monomers have been carried out with various Ni catalysts. It was found that the polymerization was affected by the structure of the ligand and the structure and the length of the monomer.

Yokozawa first applied KCGP to the synthesis of PPP (Figure 9(a)) [51]. The polymerization also followed the chain-growth mechanism with "living" feature under the optimized condition. The monomer **6** was prepared by magnesium-bromine exchange. Several Ni-complexes were employed to investigate the effect of the ligand on the polymerization. Ni(dppe)Cl_2 gave the best results. However, a salient amount of low molecular weight product was also produced. They found that the presence of the low molecular weight product could be avoided by adding 1 equiv LiCl. The polymerization proceeded faster than that without LiCl. Especially, M_n increased in proportion to the conversion of the monomer and the feed ratio of **6** to the catalyst. PPP with M_n up to 30000 and PDI < 1.2 could be prepared in a controlled fashion. It was believed that LiCl could break the

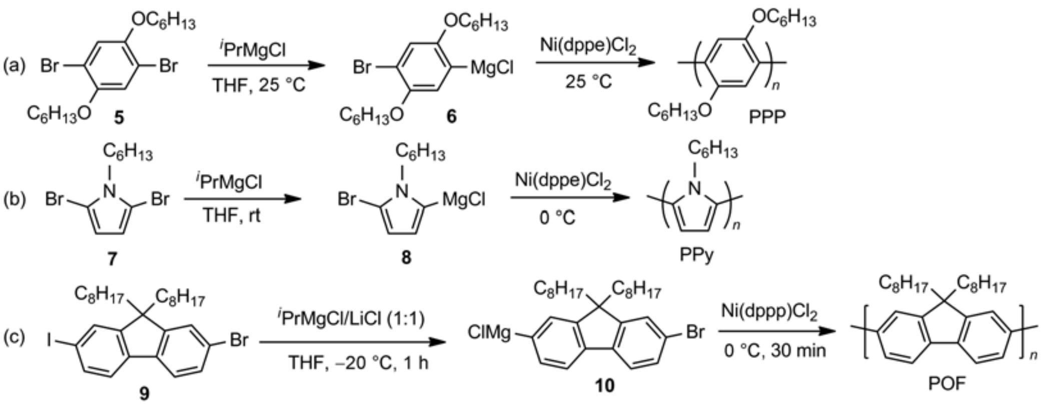


Figure 9 Kumada chain-growth polycondensations (KCGP) for PPP, PPy and POF.

aggregation of Grignard reagent to promote the polymerization.

Yokozawa *et al.* also carried out KCGP for polypyrrole (PPy, Figure 9(b)) [52]. Similar to PPP, Ni(dppe)Cl_2 was the best catalyst. The low molecular weight fraction could be avoided by adding 1 equiv dppe to the Ni catalyst. PPy with M_n of 14300 and PDI as low as 1.11 was prepared at 0 °C. The M_n also increased in proportion to the conversion of the monomer, and the polymer was dominated by Br/H chain ends as characterized by MALDI-TOF mass spectrometer. All these indicate that the polymerization exhibits the "living" feature.

Considering that intramolecular catalyst transfer is crucial to the success of KCGP, the length of the monomer may have significant effect on the polymerization. Although Kiriy *et al.* studied the polymerization of bithiophene and terthiophene monomers and concluded that the efficiency of the intramolecular catalyst transfer decreased with an increase of the number of thiophene ring, this issue has remained unraveled because they used PPh_3 as the ligand, which has been demonstrated not to be a good ligand for P3ATs [37]. Geng *et al.* systematically studied KCGP for poly(9,9-dioctylfluorene) (POF, Figure 9(c)) [53], which is one of the most important light-emitting polymers. To increase the selectivity of the magnesium-halogen exchange, 2-bromo-7-iodo-9,9-dioctylfluorene (**9**) was used as the starting compound. In the presence of LiCl, the exchange reaction was almost over in 1 h at −20 °C with a conversion up to 98%. The polymerization was carried out at 0 °C with different Ni catalysts. Ni(dppf)Cl_2 (dppf = 1,1′-bis(diphenylphosphino) ferrocene) gave no polymeric products while $Ni(PPh_3)_2Cl_2$ and Ni(dppe)Cl_2 afforded polymers with low molecular weight and broad PDI. Ni(dppp)Cl_2 gave the best results. For the polymerization with 98% conversion of **9** to **10** and 1.0 mol% Ni(dppp)Cl_2, POF with M_n of 6.24×10^4 and PDI of 1.49 was obtained with polymerization time of 30 min. The PDI is noticeably lower than that from Suzuki polycondensation. Without LiCl, the magnesium-iodine exchange reaction could still proceed but with lower conversion (77%), and the polymerization afforded lower molecular weight products with lower yields. The M_n can be tuned in the range of 1.88×10^4 to 8.60×10^4 by the feed ratio of **10** to the catalyst. Chain-growth polymerization was demonstrated by tuning the conversion of **9** to **10**. Even in the presence of ~40% **9**, the polymerization still gave high molecular weight POF, indicating a chain-growth nature of the polymerization. However, further kinetic studies indicate that the polymerization did not exhibit the "living" nature but proceeded in the way similar to the conventional radical polymerization. High molecular weight POF was obtained in the very beginning and the M_n almost kept identical at different conversions of **10**. This indicates that the polymerization follows a chain-growth mechanism, but includes chain transfer/termination. Nevertheless, compared to Suzuki polymerization, KCGP is better controlled and gives high molecular weight POF in a short time under very mild conditions. More recently, McCullough also studied the polymerization for POF starting from 2,7-dibromo-9,9-dioctylfluorene [54]. The magnesium-bromine exchange was much slower with 15% starting compound remaining after 12 h. POF with relatively low molecular weight was obtained even in the presence of crown ether 15-c-5.

Intramolecular transfer of the Ni catalyst or an associated pair formed by the growing polymer chain and Ni catalyst is believed to be essential for KCGP for conjugated polymers. It has been suggested that Ni complex could rest on the

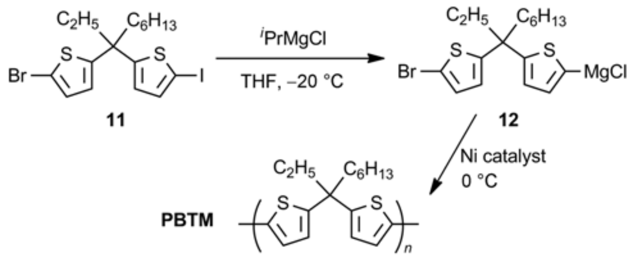


Figure 10 Kumada chain-growth polymerization for PBTM.

π-system and transfer to the chain terminus via "*ring walking*", which is the key of the efficient intramolecular catalyst transfer for KCGP [30, 31, 35]. One can imagine that the catalyst may be able to transfer across the neighboring aromatic rings that are nonconjugated but appropriately arranged in space, thus KCGP is also applicable to the synthesis of nonconjugated polymers. Geng *et al*. demonstrated this speculation with a bithienylmethane derivative (**12**) as the monomer, in which two thiophene rings are connected via a saturated carbon (Figure 10) [55]. They found that both Ni(dppp)Cl_2 and Ni(dppe)Cl_2 gave poly(bithienylmethylene) (PBTM) with narrow PDI. The polymerization proceeded too fast and was over in 0.5 min with Ni(dppp)Cl_2 (2 mol%) as the catalyst. With Ni(dppe)Cl_2 (2 mol%) as the catalyst, the polymerization afforded PBTM with narrow PDI of 1.28 and M_n of 1.28×10^4, which are close to the theoretical value. The polymerization rate was moderate with a conversion of 91% in 70 min. M_n to conversion was linear over the whole polymerization process. Moreover, the M_n of PBTM was controlled by tuning feed ratios of **12** to the catalyst with M_n up to 5.51×10^4 and PDI $\leqslant$ 1.28. The "living" nature of the polymerization was also demonstrated by block copolymerization. When Grignard reagent **2** was added into the polymerization mixture of **12**, a diblock copolymer comprising PBTM and P3HT blocks could be prepared, indicating that the PBTM chain is active and initiates the polymerization of **2**. This finding implies that KCGP is a universal method for the preparation of polymers based on aromatic units with a diversity of structures.

5 Surface-initiated polymerization and polymer brushes

Polymer brushes formed on a solid surface are attractive due to their various potential applications. Surface initiated "graft-from" polymerization is an efficient protocol to prepare polymer brushes in a well-controlled way. However, step-growth polymerizations generally used for preparation of conjugated polymers are hardly applicable for this purpose. Instead, recently developed KCGP provides an appropriate method to synthesize polymer brushes based on conjugated polymers. The critical step to realize this aim is how to load the catalyst on the solid surface.

As mentioned in Figure 6, Ar-NiL_2-X complexes can be prepared by oxidative addition of Ni(0) to the aryl halide. Therefore, this type of Ni-initiator should be loaded on the surface attached with Ar-X moieties. Kiriy *et al*. first demonstrated the P3HT brushes on poly(4-bromostyrene) (PS(Br))-coated Si wafers [56, 57]. PS(Br) layer was photo-cross-linked before polymerization. A 2 nm poly(glycidyl methacrylate), which reacts with the Si surface upon thermal annealing (10 h at 150 °C in argon) and with PS(Br) upon UV-irradiation, was used as an adhesion layer to avoid the delamination. The resulting PS(Br) layer was insoluble but swellable. Treatment of the films with $Ni(PPh_3)_4$ solution afforded the films containing Ph-$Ni(PPh_3)_2$-Br initiator. It was found that ~16% of all Br reacted with the catalyst by X-ray photoelectron spectroscopy. The subsequent surface-initiated polymerization at 0 °C gave the P3HT brushes with various thicknesses. However, the thickness of the grafted P3HT increased nearly in proportion to the thickness of PS(Br) layer. Careful studies indicate that the polymerization followed an "interpenetrated network" model, as shown in Figure 11 [57]. That means the polymerization proceeds not only from the topmost layer, but also from the inner layer, because the swellability of the PS(Br) film allows both $Ni(PPh_3)_4$ and the monomer diffusing into the inner layer to produce the initiator and polymerize, respectively. Moreover, because of the significant chain-termination for Ph-$Ni(PPh_3)_2$-Br catalyzed polymerization, P3HT grafts were only about 10 nm, corresponding to ~30 repeating units. Later, they also prepared P3HT brushes in a similar way but by using poly(4-vinylpyridine)-*block*-poly(4-iodostyrene) (P4VP-*b*-PS(I)) instead of PS(Br) [58]. P4VP strongly absorbs to a variety of polar substrates, such as Si-wafers, glass and metal oxide surfaces, allowing the growth of the brushes. Micropatterned $P4VP_{25}$-*b*-$PS(I)_{350}$-*b*-P3HT brushes were prepared by first patterning $P4VP_{25}$-*b*-$PS(I)_{350}$ via colloidal lithography. Particularly, they also demonstrated that the nano-patterned polymer brushes could be made by spin-casting a micellar dispersion of $P4VP_{75}$-*b*-$PS(I)_{313}$ onto Si-wafers followed by subsequent surface-initiated polymerization.

The poor polymerization performance of Ph-$Ni(PPh_3)_2$-Br type catalysts could only afford the P3HT grafts with relatively short chain length due to the significant chain-termination. To solve this problem, Kiriy *et al*. developed an approach to make organosilica particles carry surface initiators, as shown in Figure 12 [59]. As discussed in the previous sections, polymerizations for P3HT catalyzed by the Ni complexes with bidentate phosphorus ligand proceed in a quasi-living manner. Accordingly, this new approach allows preparing hairy particles with densely grafted P3HT chains, the polymerization degree of which up to 250 can be achieved. They also made bulk heterojunction PSCs with

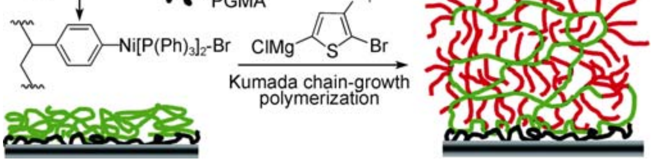


Figure 11 Schematic representation of the structure of P3HT film grafted from photo-cross-linked PS(Br) film [57].

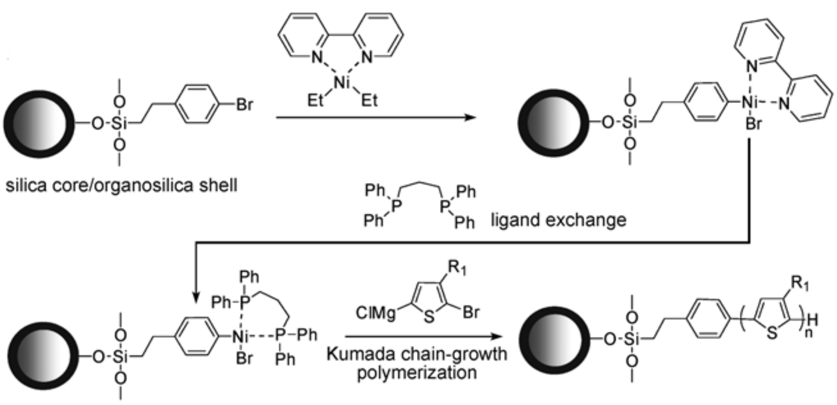


Figure 12 Preparation of hairy P3HT/organosilica particles by surface-initiated polymerization [59].

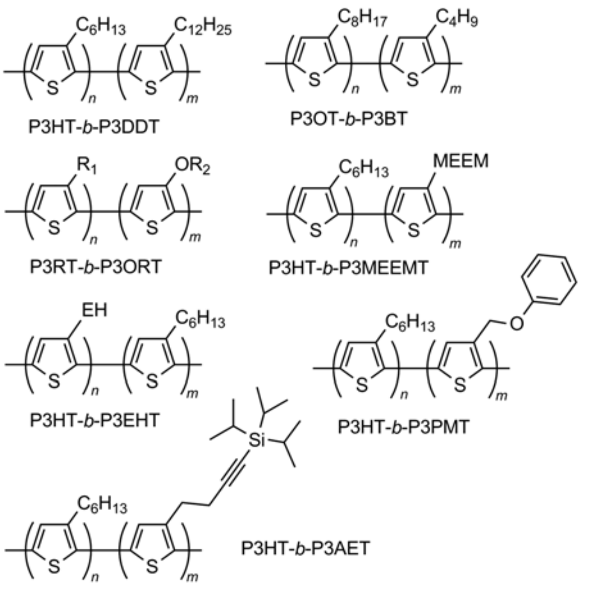
this type of hairy particles as donors. The devices showed a power conversion efficiency of 1.8%–2.3%. Surface-initiated KCGP for POF was also performed with the above organosilica particles [60]. The densely grafted POF chains prefer to adopt planar and ordered conformations even in solution compared to free POF.

Locklin *et al.* developed an alternative approach to synthesize conjugated polymer brushes via surface-initiated polymerization [61, 62]. They first functionalized the gold surface with thienyl bromide monolayers, which underwent oxidative addition with Ni(COD)$_2$ in the presence of PPh$_3$ to produce monolayers loading with Th-Ni(COD)(PPh$_3$)$_2$-Br (Th = thienyl) initiator moieties [61]. Subsequent polymerizations allowed preparing polythiophene and polyphenylene brushes with thicknesses of 10–42 nm. Later, they systematically studied the surface-initiated polymerization on silica wafer and glass substrates, and used dppe instead of PPh$_3$ as the phosphorous ligand [62]. Unlike the polymerization of **6** in bulk solution as reported by Yokozawa, they did not observe the polymer growth when 1-bromo-4-chloromagnesio-2,5-dimethoxybenzene was used as the monomer. Instead, the polymerization proceeded with 1-chloromagnesio-4-iodo-2,5-dialkyloxybenzene as the monomer. Another significant finding was that the thickness of the resulting films was strongly influenced by the side chain. The film thickness that could be achieved decreased from 26 nm to 14, 8 and 1 nm with increasing the size of the side chain from H to CH_3O, CH_3CH_2O and $C_6H_{13}O$, respectively. This indicates that the bulk side chains may hinder the polymerization on a crowded surface with densely grafted polymer chains. This problem has to be solved in the future because side chains are usually necessary to render the conjugated polymer solubility.

6 Fully conjugated block copolymers

Block copolymers are able to self-organize into microphase-separated nanostructures driven by the immiscibility or the crystallinity difference between the two blocks. With the impact of the morphology and nanostructures on the optoelectronic properties of conjugated polymers, the design and synthesis of block copolymers based on conjugated blocks have been active research topics for a long time [63]. However, because the synthesis of conjugated polymers in a well-defined way was a great challenge due to lack of appropriate methods, the topics had remained unattractive before the realization of quasi-“living” chain growth polymerization for conjugated polymers.

As evidence of chain-growth polymerization with the “living” nature, the potential of KCGP for synthesizing fully-conjugated block copolymers (FCBP) has been demonstrated in Yokozawa’s report in 2004 [14]. In 2005, McCullough *et al.* first demonstrated the synthesis of polythiophene-based FCBP, P3HT-*b*-poly(3-dodecylthiophene) (P3DDT), with PDI around 1.4 [31]. The copolymerization was not perfect due to the formation of dead or inactive chains, as indicated by the presence of a low molecular weight tail in GPC profile. Using **1** instead of **1′** (Figure 4) as the starting material afforded better results. Later, different FCBPs with polythiophene backbone (Figure 13) were synthesized by several groups. Yokozawa *et al.* studied the copolymerization for P3HT-*b*-P3MEEMT [64]. They found that both the monomer addition order and the catalyst noticeably affected the copolymerization. When MEEM-substituted monomer (MEEMT) was polymerized as the first stage, two peaks were observed in GPC profiles after copolymerization, indicating the presence of inactive chains in the polymerization of MEEMT. The most successful copolymerization was carried out with Ni(dppe)Cl$_2$ as the catalyst and the monomer addition order of **2** and then MEEMT. The PDI was fairly large compared to P3HT homopolymer probably because Ni(dppe)Cl$_2$ was not the best catalyst for P3HT. FCBPs P3HT-*b*-P3EHT and P3HT-*b*-P3PMT, both comprising a crystalline block and a non-crystalline block, were prepared by Ueda’s and Hashimoto’s groups, respectively [44, 65]. Both copolymers exhibited a micropase-separated nanostructure as characterized



R_1 = 3(*S*), 7-dimethyloctyl or 3(*R*), 7-dimethyloctyl

R_2 = 3(*S*), 7-dimethyloctyl or n-octyl

EH = 2-ethylhexyl

MEEM = [2-(2-methoxyethoxy)ethoxyl]methyl

Figure 13 Structures of fully conjugated diblock copolymers comprising polythiophene backbone.

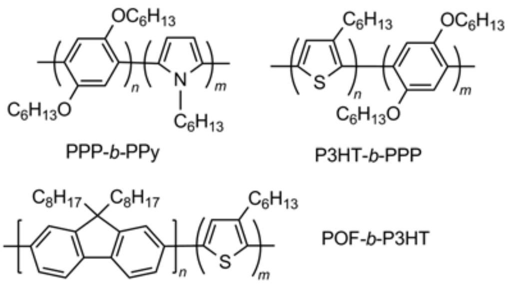


Figure 14 Structures of fully conjugated diblock copolymers comprising different conjugated blocks.

by differential scanning calorimetry (DSC) and atomic force microscopy (AFM). Very interestingly, the presence of the P3EHT block could enhance the interchain interactions of the P3HT block [65]. Crystalline-crystalline FCBP P3OT-*b*-P3BT was synthesized by Jenekhe *et al.* [66]. In the melt phase, it could assemble into a microphase-separated lamellar structure with two crystalline domains. Polythiophene-based FCBPs with one block carrying functional groups, such as P3RT-*b*-P3ORT and P3HT-*b*-P3AET, were prepared for studying supramolecular chirality or post-functionalization [46, 67]. FCBP with naphthalimide moieties in side chains was prepared from P3HT-*b*-P3AET via “click” chemistry method [46].

FCBPs comprising the blocks with different conjugated backbones are more attractive. PPP-*b*-PPy and P3HT-*b*-PPP have been prepared (Figure 14). Copolymerization for PPP-*b*-PPy is the most successful because Ni(dppe)Cl_2 is the best catalyst for both PPP and PPy. Polymerization of phenylene monomer first gave better results because polymerization of pyrrole monomer was accompanied by the trace disproportionation side-reaction [52]. The synthesis of P3HT-*b*-PPP is more complicated, which was first studied by Yokozawa *et al.* [68]. They found that only polymerizing phenylene monomer at the first stage could afford P3HT-*b*-PPP no matter Ni(dppp)Cl_2 or Ni(dppe)Cl_2 was used as the catalyst. Computer calculation indicates that the π-donor ability of P3HT was higher than that of PPP, which prohibited efficient catalyst transfer from P3HT block to phenylene segment to form block copolymers. Later, Geng *et al.* further systematically studied the block copolymerization for P3HT-*b*-PPP [34]. Although LiCl was added in the polymerization for both blocks, results were very similar to Yokozawa’s. The copolymerization mixture with the monomer addition order of thiophene and then phenylene monomers was fractioned by preparative GPC. MALDI-TOF mass spectroscopic analysis of the fractions indicates that the deactivated polymer chains mainly contained phenyl end-capped P3HT, implying inefficient catalyst transfer from P3HT block to phenylene terminus. Moreover, PPP-*b*-P3HT diblock copolymers with different block ratios were synthesized. The crystalline-crystalline microphase separation characteristic of the diblock copolymers were confirmed by DSC and AFM observations. More recently, McCullough *et al.* synthesized the diblock copolymer POF-*b*-P3HT with M_n of 7700 and PDI of 1.23 by carefully controlling the polymerization condition [69].

7 Rod-coil block copolymers

Rod-coil block copolymers can self-assemble into various nanostructures and thus are very attractive for many opto-electronic applications. KCGP with living characteristics enables the incorporation of various functional groups in one or two ends of the conjugated polymers deterministically by using appropriate initiators or by end-capping with functional Grignard reagents [36, 70, 71]. This allows preparing conjugated polymer-based macroinitiators (Figure 15) for atom transfer radical polymerization (ATRP) [72–75], nitroxide-mediated free radical polymerization (NMP) [76, 77], reverse addition fragmentation chain transfer polymerization (RAFT) [77], ring-opening polymerization (ROP) [78], and anionic living polymerization [79]. The terminal functionalized conjugated polymers can directly react with active polymer chains for synthesizing rod-coil block copolymers [75, 80–82]. P3HT-based block copolymers are of pursuit most actively because P3HT is one of the most promising conjugated polymers for PSCs and OTFTs.

McCullough *et al.* reported the preparation of P3HT-*b*-PMA (PMA = poly(methyl macrylate)) with PMA up to 57%

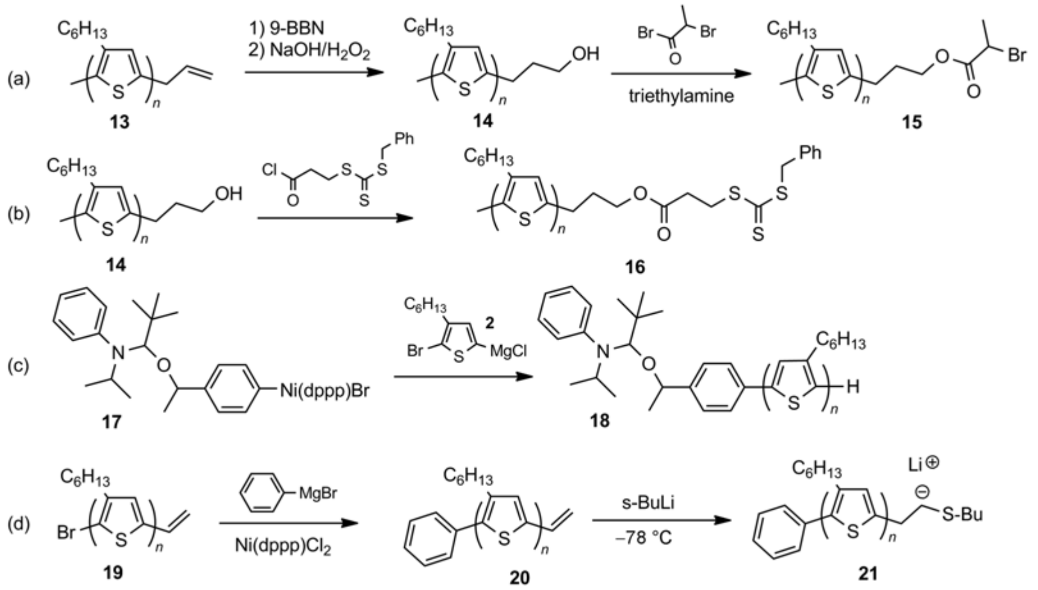


Figure 15 Preparation of macroinitiators for synthesizing P3HT-based rod-coil block copolymers.

by ATRP with a P3HT-macroinitiator, which was prepared from vinyl or allyl-terminated P3HT, as shown in Figure 15(a) [72–74]. These diblock copolymers showed good processability and could form the films showing nanofibrillar morphology. The dependence of both conductivity (doping with I_2) and field-effect mobility on PMA content was studied. It was found there was no apparent decrease of conductivity with 48% PMA [72], and field-effect mobility was still as high as 0.048 cm^2/V s with 57% PMA [73]. They also synthesized P3HT-*b*-polystyrene (PS) by ATRP [75]. PDIs of the resulting block copolymers were relatively large due to the presence of termination and chain-transfer reaction in the ATRP process. They also synthesized macroinitiators from the intermediate **14** for synthesizing P3HT-*b*-polyisoprene (PIP) and P3HT-*b*-PS by NMP and RAFT (Figure 15(b)), respectively [77].

Kiriy *et al.* developed an elegant approach for preparing P3HT-based rod-coil block copolymers via NMP (Figure 15(c)) [76]. They synthesized an external initiator **17**, which carries an NMP initiating group. The subsequent KCGP afforded the macroinitiator for the NMP of styrene. Although there was still trace amount of P3HT homopolymer as an impurity, this approach avoided the multi-step macromolecular reactions for preparing macroinitiators as shown in Figure 15(a).

Vinyl group in mono-capped P3HT can be converted to hydroxyl-terminated P3HT in a similar way as shown in Figure 15(a). Consequently, Hillmeyer *et al.* synthesized aluminium alkoxide initiators from it for ring-opening polymerization of D,L-lactide (LA) [78]. Similar to the above ATRP and NMP procedures, a small amount of P3HT homopolymer without end-capping groups was always present in the resulting P3HT-*b*-PLA block copolymers. Most interestingly, the PLA segment could be decomposed in the presence of strong bases to afford nanoporous films. This phenomenon indicates the occurrence of phase separation, and the resulting nanoporous films might be useful in preparation of organic electronic devices. In a similar way, PLA-*b*-P3AT-*b*-PLA triblock copolymers were synthesized from P3AT decapped with hydroxyl groups [83].

P3HT-*b*-poly(2-vinylpyridine) (P2VP) rod-coil diblock copolymers were prepared by anionic polymerization with a P3HT-based organo-lithium compound (Figure 15(d)) as the initiator [79]. About 20% P3HT homopolymers could be removed through an extraction process to afford the pure block copolymers with PDIs < 1.3 and P3HT wt% as low as 14%. Depending on the content of P3HT, the copolymers could self-assemble into micelles or spheres, hexagonal close packed cylinders, lamellar, and filament-like or nanofiber structures.

Various block copolymers were prepared with terminal-functionalized P3HT as the macromolecular reactants. For example, P3HT-*b*-PS with a better controlled structure was prepared by the anionic coupling procedure [75]. In this way, the poly(styryl)lithium was first synthesized by living anionic polymerization. Then the diblock copolymer was prepared by the reaction of H/ally-terminated P3HT and this active PS. In a similar way, Ueda *et al.* synthesized PS-*b*-P3HT-*b*-PS triblock copolymers from diphenylethylene terminated P3HT [80], and Kim *et al.* synthesized P2VP-*b*-P3HT-*b*-P2VP and PIP-*b*-P3HT-*b*-PIP triblock copolymers from aldehyde-terminated P3HT [84]. Allyl-terminated P3HT was used as a chain-transfer agent in ruthenium-catalyzed ring-opening metathesis polymerization of cyclooctene. The resulting block copolymers were hydrogenated to yield P3HT-*b*-polyethylene (PE) crystalline-crystalline diblock copolymers [81]. P3HT-*b*-PS and PS-*b*-P3HT-*b*-PS block copolymers were prepared by "click" chemistry from ω-ethynyl-terminated P3HT and α,ω-pentynyl-terminated P3HT [82].

Various P3HT-based rod-coil block copolymers with functional coil segments (Figure 16) were synthesized and systematically investigated inspired by the construction of the films comprising well-defined donor-acceptor nanostructures for bulk heterojunction PSCs [85–88]. The devices of PDA-3 exhibited a power conversion efficiency (PCE) of 0.49% upon annealing at 150 °C for 20 min. This efficiency is much higher than that of the corresponding blend. Fréchet et al. found that the efficiency of solar cells of P3HT and perylene diimide could be significantly improved by adding PDA-4 as a compatibilizer. A PCE of 0.55% was achieved.

8 Summary and outlook

In summary, KCGP has become a universal method for the synthesis of conjugated polymers with a diversity of structures. Quasi-"living" polymerization has been demonstrated for some conjugated polymers, such as P3ATs, PPP and PPy. Utilizing quasi-"living" chain-growth mechanism, conjugated homopolymers with well controlled molecular weights and chain-ends, polymer brushes, and fully conjugated block copolymers have been synthesized. Rod-coil diblock and triblock copolymers were synthesized with terminal-functionalized conjugated polymers as the macroinitiators or macro-reactants. However, this method is still in a developing course, and several key issues remain. (1) What are the key factors affecting intramolecular catalyst transfer? There is still noticeable chain transfer/termination in KCGP for the conjugated polymers that have been studied, especially for those with repeating units comprising more than one aromatic ring. Successfully answering this question will help people to develop new catalysts for realizing or improving "living" of the polymerization. (2) How to synthesize fully conjugated random copolymers and diblock and triblock copolymers? Only several diblock copolymers composed of different conjugated backbones have been synthesized. The catalyst transfer efficiency between different monomer units needs to be improved for synthesizing triblock copolymers. (3) What are the new applications of KCGP? Synthesis of conjugated polymer brushes is one of the attractive topics. However, its future development needs a clear application target. Nevertheless, KCGP will provide various new polymers with well-defined architectures for understanding the structure-property relationship of conjugated polymers, constructing novel functional nanostructures, and improving the performance of optoelectronic devices.

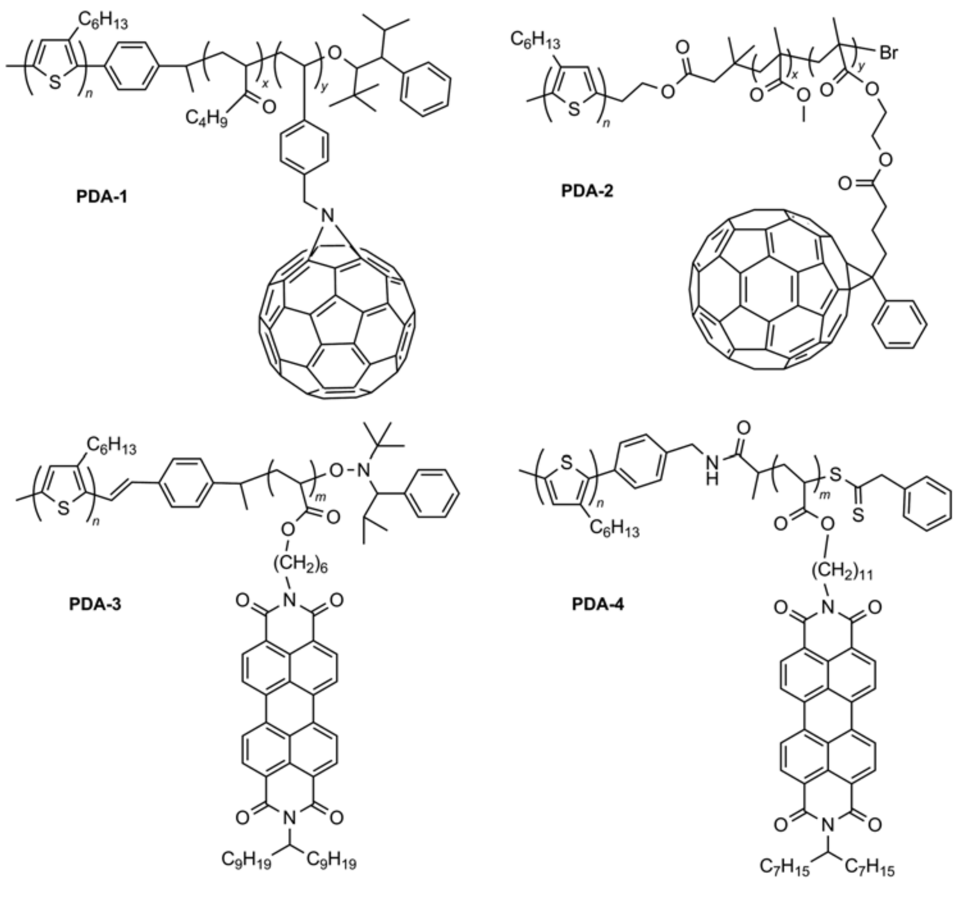


Figure 16 Donor-acceptor block copolymers prepared from P3HT macroinitiators.

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