Polymer Journal (2018) 50:475–483
https://doi.org/10.1038/s41428-018-0039-5

FOCUS REVIEW

Direct arylation polycondensation as conjugated polymer synthesis methodology

Kazuhiro Nakabayashi[1]

Received: 15 January 2018 / Revised: 14 February 2018 / Accepted: 15 February 2018 / Published online: 9 April 2018

Abstract

Direct arylation polymerization (DArP), which is a cross-coupling polymerization between a dihaloarene monomer and a non-substituted arene monomer, has attracted widespread attention for conjugated polymer synthesis. In DArP, no prior preparation of arene monomers with organometallic functionalities is necessary, in contrast to typical cross-coupling polymerizations such as the Suzuki and Stille reactions. Furthermore, the low toxicity of the byproducts of DArP contributes to green chemistry. In terms of efficiency and environmental friendliness, these advantages make DArP an attractive next-generation polymer synthetic method. To date, numerous conjugated polymers have been synthesized by DArP. However, many problems remain to be overcome, including better understanding of the correlation between polymer structure and DArP factors, the design of a more efficient DArP system, and so on. Addressing these problems could lead to the establishment of DArP as a viable alternative for conjugated polymer synthesis. We revealed that a variety of conjugated polymers such as donor–acceptor alternating copolymers (arylene diimide-based donor–acceptor alternating copolymers and thienoisoindigo-based donor-acceptor alternating copolymers) and regioregular poly(3-alkylselenophene)s were successfully synthesized by the DArP strategy based on appropriate molecular design and adjustment of the catalytic system. This focus review will describe our recent studies developing the synthesis of novel conjugated polymers via DArP.

Introduction

Conjugated polymers are important materials for next-generation electronics, such as organic field-effect transistors (OFETs), organic photovoltaics (OPVs), non-volatile organic memory, and so on [1–4]. In general, conjugated polymers are synthesized by cross-coupling polymerization between a dihaloarene monomer and an organometallic arene monomer, such as Suzuki and Stille cross-coupling polymerizations (Fig. 1) [5–7]. Cross-coupling polymerization has clearly played an essential role in the development of conjugated polymers. However, these techniques have drawbacks, such as the requirement for the prior preparation of monomers with organometallic functionalities, the toxicity of the byproducts, the low atom economy, and so on. A new methodology for the synthesis of conjugated polymers that can overcome such drawbacks is greatly needed in terms of green chemistry.

Direct arylation polymerization (DArP), cross-coupling polymerization between a dihaloarene monomer and a non-substituted arene monomer, is of current interest as a promising alternative methodology [8–12]. The synthetic advantage of DArP is that no preparation of monomers with organometallic functionality is required, which contributes to higher atom economy. Furthermore, the lower toxicity of the byproducts makes DArP more environment-friendly than conventional cross-coupling polymerizations. Since the first report of DArP, in which poly(3-alkylthiophene)s were synthesized from 2-iodo-3-alkylthiophenes [13], a variety of conjugated polymers have been synthesized by DArP [14–24]. Nevertheless, there are still many conjugated polymers that cannot be synthesized by DArP. This fact implies that DArP may currently be less universally applicable than conventional cross-coupling polymerizations, and more research is essential to expand its potential. This focus review describes our recent studies on the

✉ Kazuhiro Nakabayashi
nakabayashi.k@yz.yamagata-u.ac.jp

[1] Graduate School of Organic Materials Science, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan

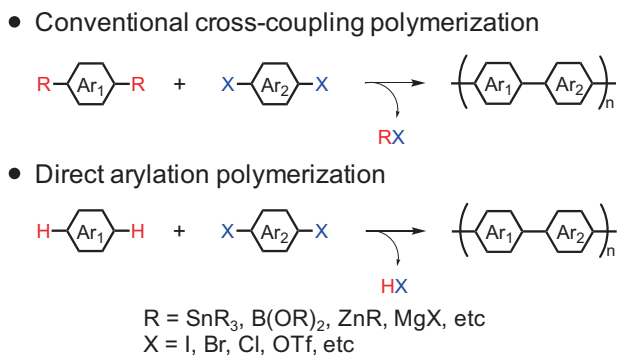

Fig. 1 General scheme of conventional cross-coupling polymerization and direct arylation polymerization (DArP)

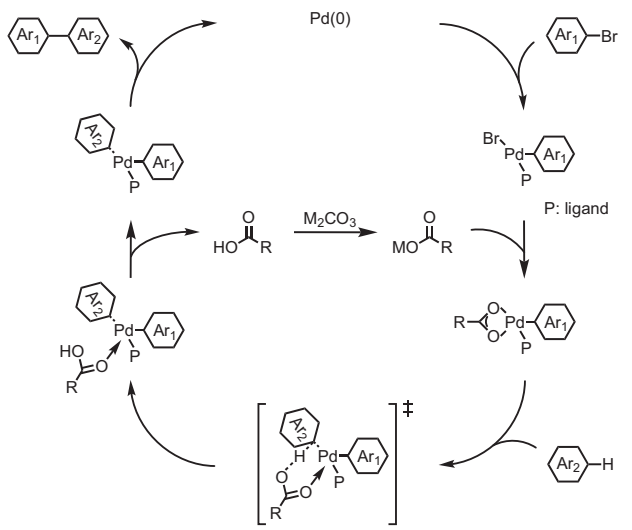

Fig. 2 Catalytic cycle of direct arylation in carboxylate-mediated conditions

development of novel conjugated polymer synthesis by DArP, which emphasizes the potential of DArP as an alternative methodology for the synthesis of conjugated polymers.

Mechanism of direct arylation

Figure 2 shows the catalytic cycle of direct arylation under carboxylate-mediated conditions, which is commonly used for the direct arylation synthesis of conjugated polymers [25]. In this cycle, the oxidative addition of palladium to a haloarene monomer occurs as well as conventional cross-coupling reactions. With assistance from the carboxylate ligand, the unsubstituted monomer is deprotonated simultaneously with the formation of the metal–carbon bond. Reductive elimination then occurs to afford the final product. The combination of reagents (i.e., palladium catalyst, phosphine ligand, acid, base, and solvent) dominates the progress of the reaction, and exploring suitable

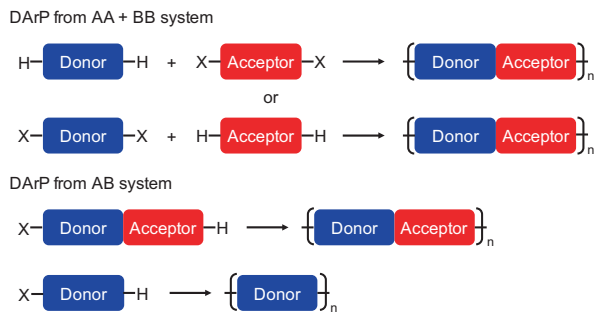

Fig. 3 Synthetic approach to obtain conjugated polymers by DArP

combinations of these reagents is a fundamental approach for DArP [26–28].

Donor–acceptor (D–A) alternating copolymers from AA + BB system

D–A alternating copolymers (i.e., low-band-gap polymers) are a promising material for many device applications because the tuning of the polymer characteristics, such as optical properties, HOMO/LUMO levels, thermal properties, and crystallinity, can be accomplished by the combination of donor and acceptor structures [29–31]. Alternating copolymerization of the bifunctional donor and acceptor monomers (AA + BB system) enables the systematic synthesis of a series of low-band-gap polymers. To date, various low-band-gap polymers have been synthesized by DArP in an AA + BB system (Fig. 3) [16, 17, 20, 22–24].

The arylene diimide (naphthalene diimide, perylene diimide, and so on) structure is a potential acceptor component because of its high electron affinity, high electron mobility, and high stability [32]. In particular, naphthalene diimide (NDI)-based low-band-gap polymers have been widely investigated as *n*-type semiconducting materials for OFETs [33–35]. In addition to OFET applications, the potential of NDI-based low-band-gap polymers as acceptor materials is also demonstrated by their use in non-fullerene solar cells (i.e., all-polymer solar cells) [36, 37]. This utility indicates that NDI-based low-band-gap polymers are high-performance acceptor polymers. Accordingly, there has been great scientific interest in and high demand for the synthesis of such high-performance acceptor polymers via DArP; however, the synthesis of arylene diimide-based low-band-gap polymers via DArP had never been accomplished.

The direct arylation synthesis of NDI-based low-band-gap polymers was firstly reported in 2012 by Horie et al. [38]. This direct arylation was carried out between a conventional dibromo NDI monomer (*N,N′*-di-*n*-hexadecyl-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid diimide) and 4,4′-bis(2-ethylhexyl)dithieno[3,2-*b*:2′,3′-*d*]silole in the presence of $Pd(OAc)_2$, which is commonly used as a

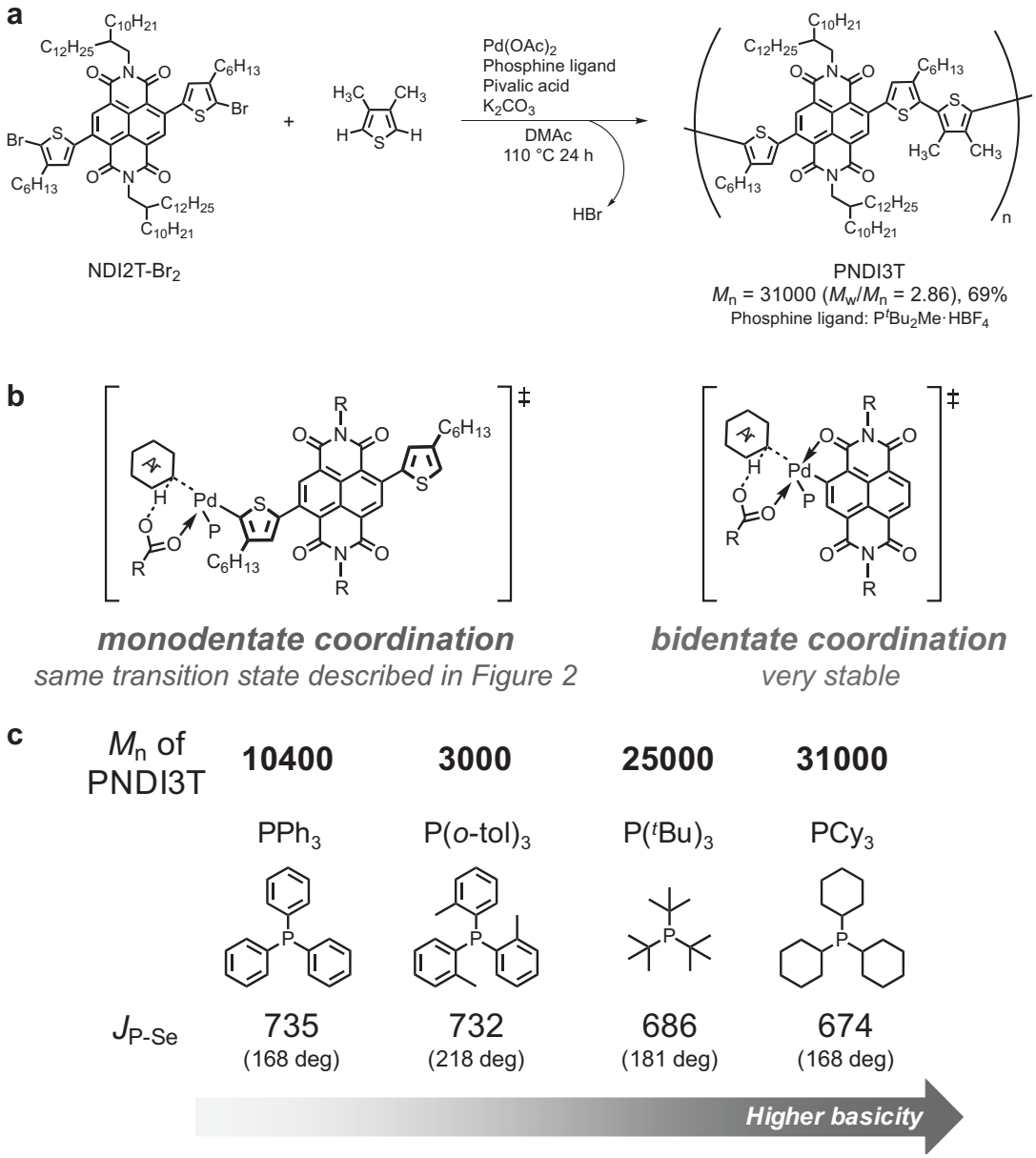

Fig. 4 **a** Direct arylation synthesis of PNDI3T from NDI2T-Br_2. **b** Two types of transition state expected from each NDI monomer. **c** Correlation between the molecular weight and phosphine ligand in PNDI3T. $J_{P\text{-}Se}$ is the coupling constant of the corresponding phosphine selenides $Se = PR_3$ (smaller values correspond to higher basicity). The cone angle (deg) of the phosphine ligand is given in parentheses

palladium catalyst in DArP. This reaction gave the corresponding polymer with a very low molecular weight ($M_n = 2200$). Due to the low reactivity of the dibromo NDI monomer, this DArP was deemed unsuccessful. Based on this result, we focused on the design of a new dibromo NDI monomer with enhanced reactivity in DArP. As explained earlier, the catalytic cycle of DArP passes through a transition state in which palladium coordinates with the carbonyl group of the carboxylate ligand. In the case of DArP using a conventional dibromo NDI monomer (e.g., *N,N′*-di-*n*-hexadecyl-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid diimide), the carbonyl group of the dibromo NDI monomer can coordinate to palladium in addition to the carboxylate ligand (Fig. 4). A very stable bidentate coordination would prevent the C–H bond cleavage. The formation of bidentate coordination is considered to be one of the reasons that DArP using a conventional dibromo NDI monomer did not proceed well. Accordingly, the design of a new dibromo NDI monomer that does not form the aforementioned bidentate coordination could be the key to the successful direct arylation synthesis of NDI-based low-band-gap polymers. Therefore, we synthesized a new dibromo NDI monomer, bromothiophene-end-capped NDI monomer (NDI2T-Br_2) [39], and investigated DArP

Table 1 Direct arylation synthesis of PNDI3T[a]

Entry	Phosphine ligand	M_n[b]	M_w/M_n[b]	Yield (%)[c]
1	$PCy_3{\cdot}HBF_4$	25,000	2.49	70
2	$P^tBu_2Me{\cdot}HBF_4$	29,000	2.04	61
3	$P^tBu_3{\cdot}HBF_4$	31,000	2.86	69
4	$P(o\text{-tol})_3$	3000	1.05	74
5	$P(o\text{-PhOMe})_3$	14,000	1.65	53
6	PPh_3	10,400	1.80	19
7	None	17000	2.67	21

[a] The detailed polymerization procedure is described in refs. [40] and [41]

[b] Determined by SEC by using polystyrene standards in chloroform

[c] Yields of chloroform-soluble fractions

between NDI2T-Br_2 and 3,4-dimethylthiophene under typical $Pd(OAc)_2$-based direct arylation conditions (Fig. 4a) [40, 41]. As shown in Table 1, the progress of DArP using NDI2T-Br_2 was significantly improved compared to the previous report, and the NDI-terthiophene alternating low-band-gap polymer PNDI3T with $M_n = 31{,}000$ was successfully obtained by using $P^tBu_3{\cdot}HBF_4$ as a result of screening phosphine ligands [41]. For comparison, DArP between *N,N′*-bis(2-decyl-1-tetradecyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid diimide and 3,4-dimethylthiophene was conducted under the same conditions; however, in this case, the polymer was not obtained. The optical, electrochemical, and thermal properties of the resulting PNDI3T were consistent with those of the corresponding polymer synthesized by Stille cross-coupling polymerization. To the best of our knowledge, DArP using NDI2T-Br_2 is the first example of the direct arylation synthesis of an NDI-based low-band-gap polymer with high molecular weight. Furthermore, the correlation between these results as a function of the phosphine ligand provided additional insight (Fig. 4b). The reactivity of the catalyst strongly depends on the cone angle and basicity of the ligand in the cross-coupling reaction [42]. In general, a large cone angle and strong basicity promote reductive elimination and oxidative addition, respectively. In DArP using NDI2T-Br_2, the basicity tended to dominate the progress of the DArP rather than the cone angle. This fact indicates that the promotion of the oxidative addition process by a ligand with strong basicity (strong electron-donation) is highly important for DArP using NDI2T-Br_2. Following our first report on DArP using NDI2T-Br_2, other research groups have developed NDI-based low-band-gap polymers by this approach, thus showing its general versatility [43–45]. It should be noted, however, that Sommer et al. developed the direct arylation synthesis of NDI-based low-band-gap polymers from a conventional dibromo NDI monomer while exploring the Pd_2dba_3-based catalytic system [46].

In addition, perylene diimide (PDI)-based low-band-gap polymers were successfully synthesized by using a bromothiophene-end-capped PDI monomer (PDI2T-Br_2) [47]. The results of condition screening showed that the tendency of suitable phosphine ligands for DArP with the PDI monomer was similar to that with the NDI monomer; a PDI-terthiophene alternating low-band-gap polymer PPDI3T with $M_n = 13{,}600$ was obtained in the presence of $PCy_3{\cdot}HBF_4$ with strong basicity (Fig. 5a). Furthermore, random copolymerization of NDI2T-Br_2, PDI2T-Br_2, and 3,4-dimethylthiophene successfully afforded the random copolymer with NDI and PDI components, P(NDI3T-PDI3T), and the component ratio (*m/n*) could be tuned by adjusting the feed ratios of NDI2T-Br_2 and PDI2T-Br_2 (Fig. 5b). The light harvesting property was tuned in the range of 400–800 nm by adjusting the *m/n* component ratio.

D–A alternating copolymers from AB system

The synthesis of low-band-gap polymers by using an AA + BB system is a good method in terms of systematic sample preparation. On the other hand, a common problem in the AA + BB system is that undesirable side reactions due to homo-couplings might occur [48, 49]. It is possible to minimize such structural defects by optimizing the reaction conditions in the AA + BB system [50, 51]. However, DArP using an asymmetric AB-type monomer (i.e., self-condensation-type DArP) could be a more effective way to fundamentally avoid this drawback. Furthermore, strict stoichiometric control can also be avoided in the AB system. Therefore, self-condensation-type DArP is more attractive than DArP in the AA + BB system from a practical point of view. However, the synthesis of low-band-gap polymers via self-condensation-type DArP is far less developed than that via DArP in the AA + BB system. Therefore, we investigated the synthesis of low-band-gap polymers via self-condensation-type DArP. Our designed NDI monomer end-capped with thiophene was considered a monomer with the D–A architecture. The self-condensation-type DArP using an asymmetric NDI-based D–A monomer NDI2T-Br was investigated (Fig. 6a) [52]. The combination of reagents (palladium catalyst, phosphine ligand, base, and solvent) for polymerization was optimized based on the direct arylation synthesis of NDI-based low-band-gap polymers described earlier. As a result, the NDI-dithiophene alternating low-band-gap polymer PNDI2T with the highest M_n ($M_n = 13{,}000$) was obtained in high yield under the $Pd(OAc)_2/PCy_3{\cdot}HBF_4/K_2CO_3$/PivOH/DMAc condition.

The thienoisoindigo (TIG) structure has been investigated intensively as a new class of acceptor components for low-band-gap materials [53]. The high molecular ordering,

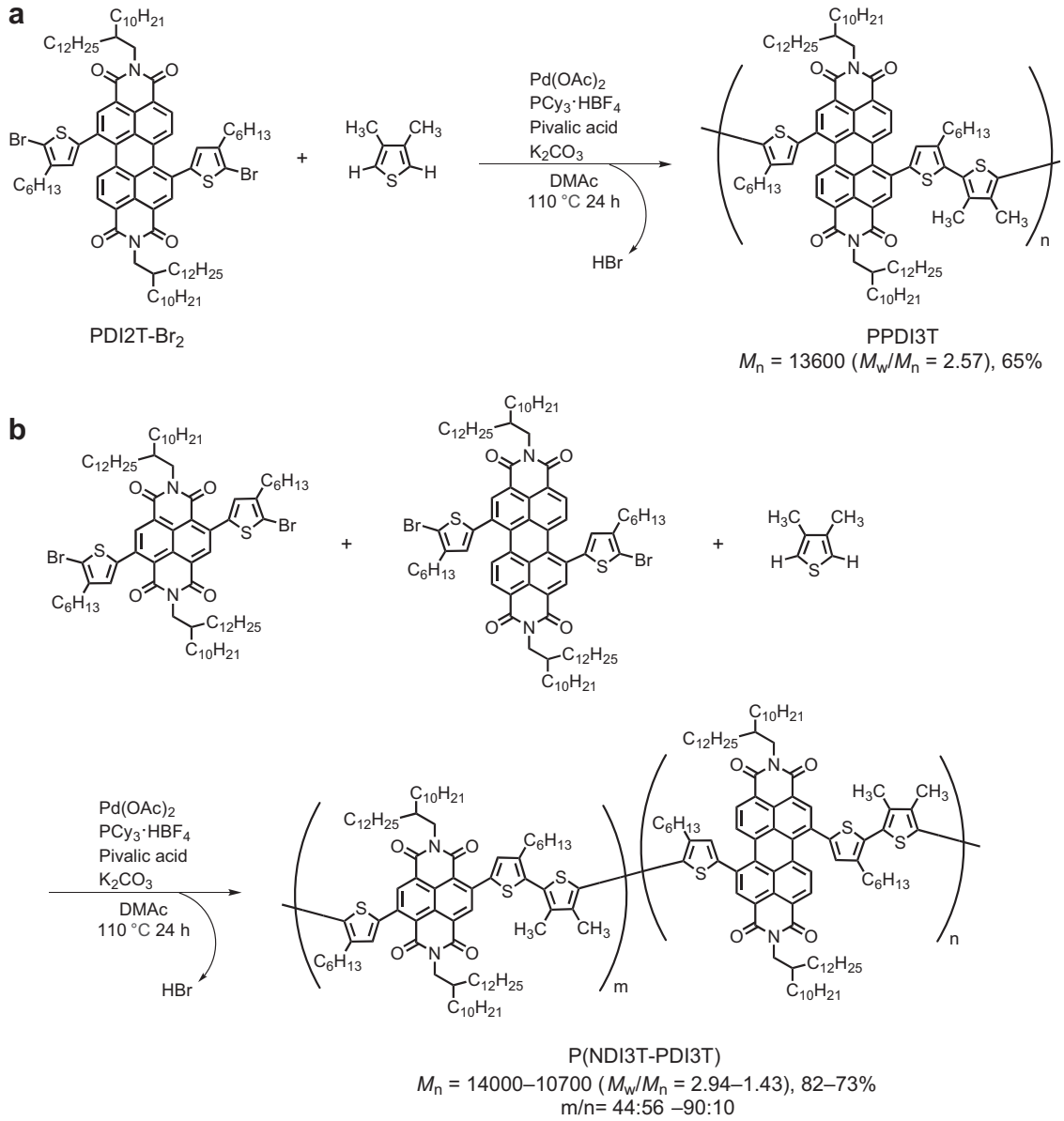

Fig. 5 Direct arylation synthesis of (**a**) PPDI3T and (**b**) P(NDI3T-PDI3T)

expanded π-conjugation, and efficient charge transport due to the high coplanarity via S…O interactions, and the high charge delocalization via the quinoidal structure of the backbone are characteristics of the TIG structure. By utilizing these advantages, an OFET with a TIG-based low-band-gap polymer achieved ultrahigh hole mobility above 14 $cm^2/V{\cdot}s$ [54]. showing the high potential of TIG-based low-band-gap polymers for opto-electrical applications. We herein investigated the direct arylation synthesis of new TIG-based low-band-gap polymers from an asymmetric TIG-based D-A monomer TIG2T-Br [55]. By optimizing the reaction conditions, a TIG-dithiophene alternating low-band-gap polymer PTIG2T with $M_n = 8300$ was obtained in the presence of $Pd_2dba_3/P^tBu_2Me{\cdot}HBF_4/K_2CO_3$/PivOH in toluene (Fig. 6b). The direct arylation synthesis of TIG-based low-band-gap polymers by the AA + BB system was reported by Wang et al. and Mei et al.; however, the polydispersities of the obtained polymers were relatively high in some cases, implying some undesirable side reactions [56, 57]. Furthermore, we investigated the photovoltaic property of a PTIG2T:$PC_{61}BM$ active layer in a conventional device configuration of ITO/PEDOT:PSS/PTIG2T:$PC_{61}BM$/Ca/Al. A power conversion efficiency (PCE) of 3.19% was achieved with a V_{oc} of 0.52 V, J_{sc} of 10.58 mA/cm^2, and FF of 0.58. TIG-based low-band-gap materials synthesized by conventional cross-coupling

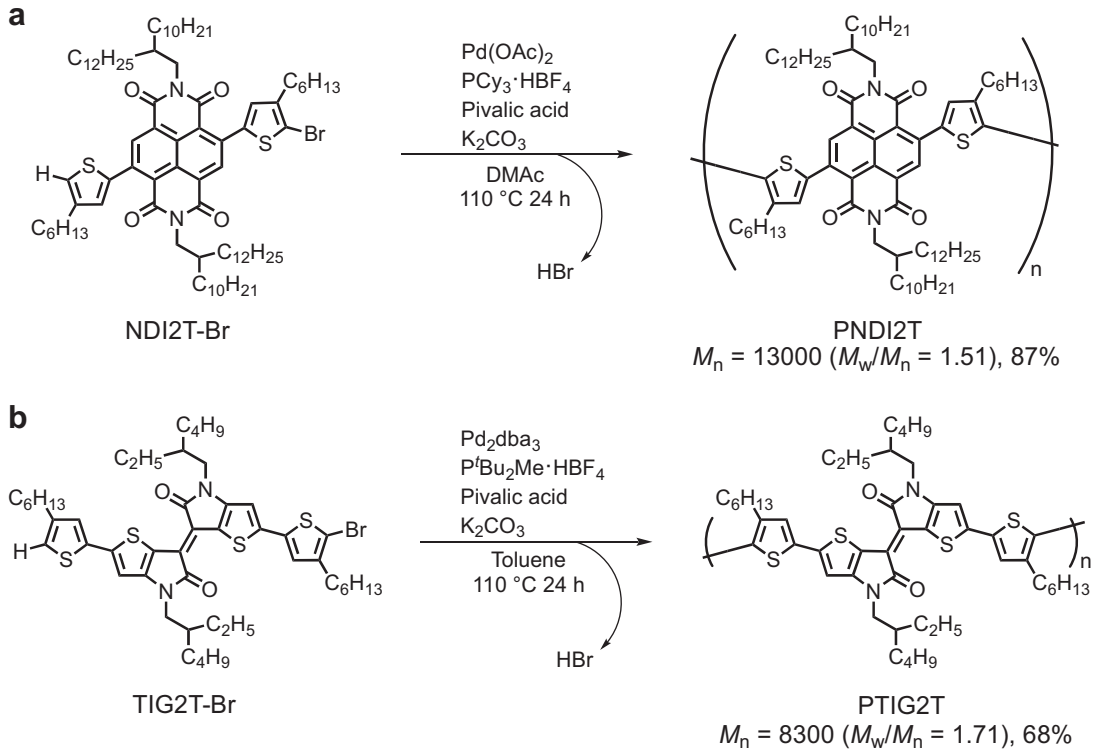

Fig. 6 Direct arylation synthesis of (**a**) PNDI2T and (**b**) PTIG2T from asymmetric D–A monomer

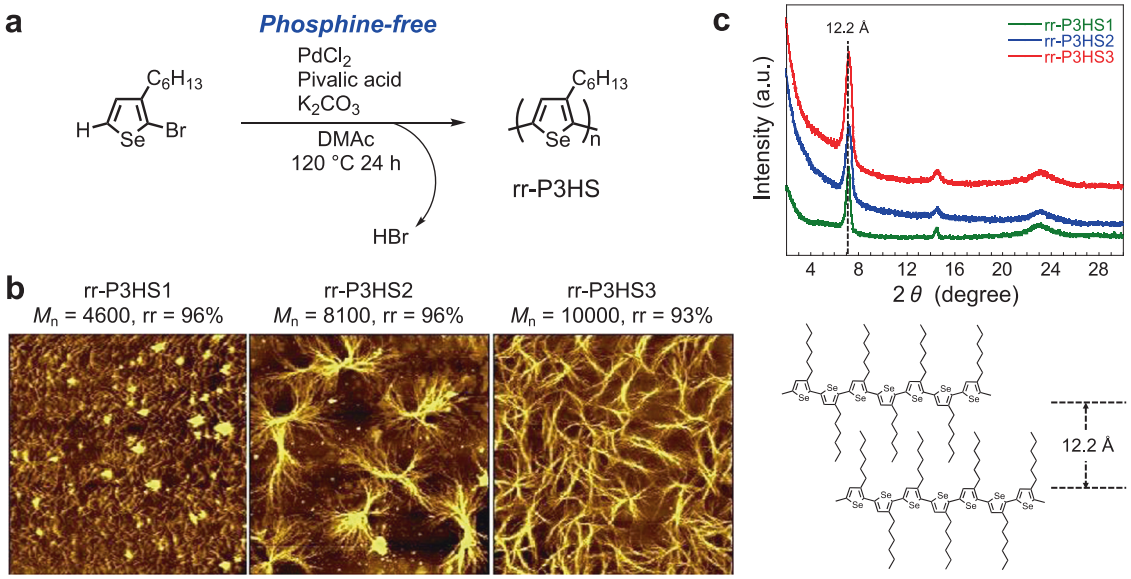

Fig. 7 **a** Direct arylation synthesis of rr-P3HS. **b** Topographic AFM images (30 × 30 μm) of drop-cast rr-P3HS films prepared from chlorobenzene solutions. **c** XRD profiles of drop-cast rr-P3HS films prepared from chlorobenzene solutions

reactions have been used in OPVs as donor materials; most of those OPVs exhibited PCE values of 1–3% [58–60]. The PCE of 3.19% from PTIG2T was one of the highest PCEs achieved by OPVs with TIG-based low-band-gap materials. Furthermore, this fabricated OPV is the first example that used a TIG-based low-band-gap material synthesized via DArP. These results demonstrate that a TIG-based low-band-gap polymer obtained by DArP can be utilized for

OPV applications as effectively as those synthesized via conventional cross-coupling reactions.

Regioregular polyselenophenes from AB system

We are currently interested in polyselenophenes. Polyselenophenes have comparable HOMO levels to those of polythiophenes, while the LUMO levels of polyselenophenes are lower than those of polythiophenes [61–63]. Therefore, it is expected that polyselenophenes have the reduced optical band gaps, enhanced photostability, and improvement of electron transportation compared to polythiophenes. Considering these advantages, polyselenophenes have the potential to be more promising materials for organic electronics than polythiophenes. Nevertheless, studies of polyselenophenes, covering the synthesis, characterization, morphological analysis, and device applications, are far less developed than the research on polythiophenes. As for the synthesis of poly(3-alkylselenophene) which is one of basic polyselenophenes, oxidative polymerization [64], and Grignard-metathesis (GRIM) polymerization [62] have been reported. Unfortunately, the feature of the polymer structure, such as molecular weight, polydispersity, reaction sites, and so on, could not be controlled by oxidative polymerization. GRIM polymerization requires completely anhydrous reaction conditions to obtain regioregular poly(3-alkylselenophene)s with high molecular weight ($M_n > 10{,}000$) and narrow polydispersity ($M_w/M_n < 1.2$). Accordingly, there is a great need to develop more facile and efficient methods to synthesize polyselenophenes. We successfully synthesized regioregular poly(3-hexylselenophene) rr-P3HS (regioregularity: rr = 92–96%) under the simple phosphine-free DArP condition by using $PdCl_2$ as a catalyst (Fig. 7a) [65]. The effectiveness of $PdCl_2$ under the phosphine-free condition can be explained by the previously reported chloride-promoted direct arylation mechanism; chloride ion acted as a ligand, resulting in an efficient concerted metalation-deprotonation catalytic cycle [66]. Cheng et al. recently reported the synthesis of rr-P3HS via DArP under $Pd(OAc)_2$-based conditions; however, both the molecular weight and the regioregularity were lower than those we obtained [67]. This fact supports the advantage of $PdCl_2$ for the phosphine-free direct arylation synthesis of rr-P3HS. The assembly of nanofibers was observed by atomic force microscopy, and the assembly behavior (e.g., forming non-woven fibrous and bundle-like spherulitic self-assembled nanostructures) depended on the molecular weight of rr-P3HS (Fig. 7b). Furthermore, according to X-ray diffraction analysis, the formation of fibrous nanostructures was attributed to the pure crystalline structure with significant interdigitation of the hexyl side chains (Fig. 7c).

Conclusions

DArP is a promising candidate for an alternative method of synthesizing conjugated polymers in terms of efficiency and environmental friendliness. We developed a direct arylation methodology using acceptor monomers end-capped with electron-rich units (e.g., D–A monomers for AA + BB and AB system, respectively). By using these newly designed monomers under optimized direct arylation conditions, a variety of low-band-gap polymers, including NDI, PDI, and TIG-based low-band-gap polymers, were successfully synthesized. Furthermore, the direct arylation synthesis of rr-P3HS (rr = 92–96%) was achieved under $PdCl_2$-based phosphine-free conditions. Our results demonstrate that DArP yields various desirable conjugated polymers with appropriate molecular design and adjustment of the catalytic system. There is still much room to pursue fundamental research with regard to DArP. Therefore, it is expected that further development by energetic investigation will lead to greater utility of DArP as an alternative conjugated polymer synthesis methodology.

Acknowledgements I wish to thank all my colleagues for their great contributions to this focus review. The author is deeply indebted to Professor Hideharu Mori (Yamagata University) for continuous encouragement and constructive discussions. This work was supported by two Grants-in-Aid for Young Scientists (B) (26810064 and 16K17908) from the Japan Society for the Promotion of Science (JSPS), the Izumi Science and Technology Foundation, and the Iketani Science and Technology Foundation.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Günes S, Neugebauer H, Sariciftci NS. Conjugated polymer-based organic solar cells. Chem Rev. 2007;107:1324–38.
2. Boudreault PTL, Najari A, Leclerc M. Processable low-bandgap polymers for photovoltaic applications. Chem Mater. 2011;23:456–69.
3. Zhou H, Yang L, You W. Rational design of high performance conjugated polymers for organic solar cells. Macromolecules. 2012;45:607–32.
4. Chou Y-H, Chang H-C, Liu C-L, Chen W-C. Polymeric charge storage electrets for non-volatile organic field effect transistor memory devices. Polym Chem. 2015;6:341–52.
5. Miyaura N, Suzuki A. Palladium-catalyzed cross-coupling reactions of organoboron compounds. Chem Rev. 1995;95:2457–83.

6. Suzuki A. Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998. J Organomet Chem. 1999;576:147–68.
7. Corbet J-P, Mignani G. Selected patented cross-coupling reaction technologies. Chem Rev. 2006;106:2651–710.
8. Facchetti A, Vaccaro L, Marrocchi A. Semiconducting polymers prepared by direct arylation polycondensation. Angew Chem Int Ed. 2012;51:3520–3.
9. Okamoto K, Zhang J, Housekeeper JB, Marder SR, Luscombe CK. C–H arylation reaction: atom efficient and greener syntheses of π-conjugated small molecules and macromolecules for organic electronic materials. Macromolecules. 2013;46:8059–78.
10. Mercier LG, Leclerc M. Direct (hetero)arylation: a new tool for polymer chemists. Acc Chem Res. 2013;46:1597–605.
11. Kowalski S, Allard S, Zilberberg K, Riedl T, Scherf U. Direct arylation polycondensation as simplified alternative for the synthesis of conjugated (co)polymers. Prog Polym Sci. 2013;38:1805–14.
12. Pouliot J-M, Grenier F, Blaskovits T, Beaupré S, Leclerc M. Direct (hetero)arylation polymerization: simplicity for conjugated polymer synthesis. Chem Rev. 2016;116:14225–74.
13. Sévigron M, Papillion J, Schulz E, Lemaire M. New synthetic method for the polymerization of alkylthiophenes. Tetrahedron Lett. 1999;44:5873–6.
14. Wang Q, Takita R, Kikuzaki Y, Ozawa F. Palladium-catalyzed dehydrohalogenative polycondensation of 2-bromo-3-hexylthiophene: an efficient approach to head-to-tail poly(3-hexylthiophene). J Am Chem Soc. 2010;132:11420–1.
15. Lu W, Kuwabara J, Kanbara T. Polycondensation of dibromofluorene analogues with tetrafluorobenzene via direct arylation. Macromolecules. 2011;44:1252–5.
16. Kowalski S, Allard S, Scherf U. Synthesis of poly(4,4-dialkylcyclopenta[2,1-*b*:3,4-*b′*]dithiophene-*alt*-2,1,3-benzothiadiazole) (PCPDTBT) in a direct arylation scheme. ACS Macro Lett. 2012;1:465–8.
17. Berrouard P, Najari A, Pron A, Gendron D, Morin P-O, Pouliot J-R, Veilleux J, Leclerc M. Synthesis of 5-alkyl[3,4-c]thienopyrrole-4,6-dione-based polymers by direct heteroarylation. Angew Chem Int Ed. 2012;51:2068–71.
18. Rudenko AE, Wiley CA, Stone SM, Tannaci JF, Thompson BC. Semi-random P3HT analogs via direct arylation polymerization. J Polym Sci Part A Polym Chem. 2012;50:3691–7.
19. Zhao H, Liu C-Y, Luo S-C, Zhu B, Wang T-H, Hsu H-F, Yu H-H. Facile syntheses of dioxythiophene-based conjugated polymers by direct C–H arylation. Macromolecules. 2012;45:7783–90.
20. Kuwabara J, Nohara Y, Choi SJ, Fujinami Y, Liu W, Yoshimura K, Oguma J, Suenobu K, Kanbara T. Direct arylation polycondensation for the synthesis of bithiophene-based alternating copolymers. Polym Chem. 2013;4:947–53.
21. Liu D-P, Chen Q, Zhao Y-C, Zhang L-M, Qi A-D, Han B-H. Fluorinated porous organic polymers via direct C–H arylation polycondensation. ACS Macro Lett. 2013;2:522–6.
22. Zhang X, Gao Y, Li S, Shi X, Geng Y, Wang F. Synthesis of poly (5,6-difluoro-2,1,3-benzothiadiazole-alt-9,9-dioctylfluorene) via direct arylation polycondensation. J Polym Sci Part A Polym Chem. 2014;52:2367–74.
23. Dudnik AS, Aldrich TJ, Eastham ND, Chang RPH, Facchetti A, Marks TJ. Tin-free direct C–H arylation polymerization for high photovoltaic efficiency conjugated copolymers. J Am Chem Soc. 2016;138:15699–709.
24. Kojima Y, Hayashi S, Koizumi T. Palladium on carbon-catalyzed direct C–H arylation polycondensation of 3,4-ethylenedioxythiophene with various dibromoarenes. J Polym Sci Part A Polym Chem. 2017;55:1183–8.
25. Lapointe D, Fangnou K. Overview of the mechanistic work on the concerted metallation–deprotection pathway. Chem Lett. 2010;39:1118–26.
26. Rudenko AE, Thompson BC. Influence of the carboxylic acid additive structure on the properties of poly(3-hexylthiophene) prepared via direct arylation polymerization (DArP). Macromolecules. 2015;48:569–75.
27. Kuwabara J, Yamazaki K, Yamagata T, Tsuchida W, Kanbara T. The effect of a solvent on direct arylation polycondensation of substituted thiophenes. Polym Chem. 2015;6:891–5.
28. Matsidik R, Komber H, Sommer M. Rational use of aromatic solvents for direct arylation polycondensation: C–H reactivity versus solvent quality. ACS Macro Lett. 2015;4:1346–50.
29. Mühlbacher D, Scharber M, Morana M, Zhu Z, Waller D, Gaudiana R, Brabec C. High photovoltaic performance of a low-bandgap polymer. Adv Mater. 2006;18:2884–9.
30. Bundgaard E, Krebs FC. Low-band-gap conjugated polymers based on thiophene, benzothiadiazole, and benzobis(thiadiazole). Macromolecules. 2006;39:2823–31.
31. Hou J, Chen H-Y, Zhang S, Chen RI, Yang Y, Wu Y, Li G. Synthesis of a low band gap polymer and its application in highly efficient polymer solar cells. J Am Chem Soc. 2009;131:15586–7.
32. Zhan X, Facchetti A, Barlow S, Marks TJ, Ratner MA, Wasielewski MR, Marder SR. Rylene and related diimides for organic electronics. Adv Mater. 2011;23:268–84.
33. Yan H, Chen Z, Zheng Y, Newman C, Quinn JR, Dötz F, Kastler M, Facchetti A. A high-mobility electron-transporting polymer for printed transistors. Nature. 2009;457:679–86.
34. Kim FS, Guo X, Watson MD, Jenekhe SA. High-mobility ambipolar transistors and high-gain inverters from a donor–acceptor copolymer semiconductor. Adv Mater. 2010;22:478–82.
35. Szumilo MK, Gann EH, McNeill CR, Lemaur V, Oliver Y, Thomsen L, Vaynzof Y, Sommer M, Sirringhaus H. Structure influence on charge transport in naphthalenediimide−thiophene copolymers. Chem Mater. 2014;26:6796–804.
36. Hwang Y-J, Courtright BAE, Ferreira AS, Tolbert SH, Jenekhe SA. 7.7% Efficient all-polymer solar cells. Adv Mater. 2015;27:4578–84.
37. Lee C, Kang H, Lee W, Kim T, Kim K-H, Woo HY, Wang C, Kim BJ. High-performance all-polymer solar cells via side-chain engineering of the polymer acceptor: the importance of the polymer packing structure and the nanoscale blend morphology. Adv Mater. 2015;27:2466–71.
38. Chang S-W, Waters H, Kettle J, Kuo Z-R, Li C-H, Yu C-Y, Horie M. Pd-catalysed direct arylation polymerisation for synthesis of low-bandgap conjugated polymers and photovoltaic performance. Macromol Rapid Commun. 2012;33:1927–32.
39. Nakabayashi K, Mori H. All-polymer solar cells based on fully conjugated block copolymers composed of poly(3-hexylthiophene) and poly(naphthalene bisimide) segments. Macromolecules. 2012;45:9618–25.
40. Nakabayashi K, Mori H. Palladium-catalyzed direct arylation approach to synthesize naphthalene bisimide-based low-band-gap polymers. Chem Lett. 2013;42:717–8.
41. Nakabayashi K, Yamada M, Mori H. Naphthalene bisimide-based acceptor polymers: synthesis via palladium-catalyzed direct arylation, characterization, and nanostructure. Bull Chem Soc Jpn. 2015;88:222–6.
42. Ohta H, Tokunaga M, Obara Y, Iwai T, Iwasawa T, Fujihara T, Tsuji Y. A bowl-shaped phosphine as a ligand in palladium-catalyzed Suzuki−Miyaura coupling of aryl chlorides: effect of the depth of the bowl. Org Lett. 2007;9:89–92.
43. Nohara Y, Kuwabara J, Yasuda T, Han L, Kanbara T.Two-step direct arylation for synthesis of naphthalenediimide-based

conjugated polymer. J Polym Sci Part A: Polym Chem. 2014;52:1401–7.
44. Luzio A, Fazzi D, Nübling F, Matsidik R, Straub A, Komber H, Giussani E, Watkins SE, Barbatti M, Thiel W, Gann E, Thomsen L, McNeill CR, Caironi M, Sommer M. Structure−function relationships of high-electron. chem. mobility naphthalene diimide copolymers prepared via direct arylation. Chem Mater. 2014;26:6233–40.
45. Shao J, Wang G, Wang K, Yang C, Wang M. Direct arylation polycondensation for efficient synthesis of narrow-bandgap alternating D–A copolymers consisting of naphthalene diimide as an acceptor. Polym Chem. 2015;6:6836–44.
46. Matsidik R, Komber H, Luzio A, Caironi M, Sommer M. Defect-free naphthalene diimide bithiophene copolymers with controlled molar mass and high performance via direct arylation polycondensation. J Am Chem Soc. 2015;137:6705–11.
47. Nakabayashi K, Yamada M, Mori H. Perylene bisimide-based semiconducting polymers: synthesis via palladium-catalyzed direct arylation, characterization, optoelectrical properties, and nanomorphology. J Polym Sci Part A Polym Chem. 2016;54:3151–8.
48. Kowalski S, Allard S, Scherf U. Scope and limitations of a direct arylation polycondensation scheme in the synthesis of PCPDTBT-type copolymers. Macromol Rapid Commun. 2015;36:1061–8.
49. Rudenko AE, Thompson BC. Optimization of direct arylation polymerization (DArP) through the identification and control of defects in polymer structure. J Polym Sci Part A Polym Chem. 2015;53:135–47.
50. Kuwabara J, Fujie Y, Maruyama K, Yasuda T, Kanbara T. Suppression of homocoupling side reactions in direct arylation polycondensation for producing high performance OPV materials. Macromolecules. 2016;49:9388–95.
51. Wakioka M, Takahashi R, Ichihara N, Ozawa F. Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Highly Selective Synthesis of π-Conjugated Polymers with Diketopyrrolopyrrole Units. Macromolecules. 2017;50:927–34.
52. Nakabayashi K, Fukuzawa H, Yamada M, Mori H. Self-condensation-type direct arylation synthesis of naphthalene bisimide-bithiophene alternating copolymers. Microsyst Technol. 2017;23:3817–23.
53. Ashraf RS, Kronemeijer AJ, James DI, Sirringhaus H, McCulloch I. A new thiophene substituted isoindigo based copolymer for high performance ambipolar transistors. Chem Commun. 2012;48:3939–41.
54. Kim G, Kang SJ, Dutta GK, Han YK, Shin TJ, Noh YY, Yang C. A thienoisoindigo-naphthalene polymer with ultrahigh mobility of 14.4 $cm^2/V{\cdot}s$ that substantially exceeds benchmark values for amorphous silicon semiconductors. J Am Chem Soc. 2014;136:9477–83.
55. Nakabayashi K, Fukuzawa H, Fujita K, Mori H. Direct arylation synthesis of thienoisoindigo-based low-band-gap polymer from asymmetric donor–acceptor monomer. J Polym Sci Part A Polym Chem. 2018;56:430–6.
56. Huang J, Wang K, Gupta S, Wang G, Yang C, Mushrif SH, Wang M. Thienoisoindigo-based small molecules and narrow bandgap polymers synthesized via C–H direct arylation coupling. J Polym Sci Part A Polym Chem. 2016;54:2015–31.
57. You L, Chaudhry ST, Zhao Y, Liu J, Zhao X, He J, Mei J. Direct arylation polymerization of asymmetric push–pull aryl halides. Polym Chem. 2017;8:2438–41.
58. Ide M, Koizumi Y, Saeki A, Izumiya Y, Ohkita H, Ito S, Seki S. Near-infrared absorbing thienoisoindigo-based copolymers for organic photovoltaics. J Phys Chem C. 2013;117:26859–70.
59. Karakawa M, Aso Y. Narrow-optical-gap π-conjugated small molecules based on terminal isoindigo and thienoisoindigo acceptor units for photovoltaic application. RSC Adv. 2013;3:16259–63.
60. Odajima T, Ashizawa M, Konosu Y, Matsumoto H, Mori T. The impact of molecular planarity on electronic devices in thienoisoindigo-based organic semiconductors. J Mater Chem C. 2014;2:10455–67.
61. Ballantyne AM, Chen LC, Nelson J, Bradley DDC, Astuti Y, Maurano A, Shuttle CG, Durrant JR, Heeney M, Duffy W, McCulloch I. Studies of highly regioregular poly(3-hexylselenophene) for photovoltaic applications. Adv Mater. 2007;19:4544–7.
62. Kong H, Chung DS, Kang IN, Park JH, Park MJ, Jung IH, Park CE, Shim HK. New selenophene-based semiconducting copolymers for high performance organic thin-film transistors. J Mater Chem. 2009;19:3490–9.
63. Patra A, Bendikov M. Polyselenophenes. J Mater Chem. 2010;20:422–33.
64. Mahatsekake C, Catel JM, Andrieu CG, Ebel M, Mollier Y, Tourillon G. Synthese Et etude electrochimique de poly(alkyl-3 selenophenes). Phosphorus Sulfur Silicon Relat Elem. 1990;47:35–41.
65. Nakabayashi K, Otsuki N, Mori H. Phosphine-free direct arylation synthesis and self-assembled nanostructure analysis of poly(3-hexylselenophene). J Polym Sci Part A Polym Chem. 2017;55:2749–55.
66. Hayashi S, Koizumi T. Chloride-promoted Pd-catalyzed direct C–H arylation for highly efficient phosphine-free synthesis of π-conjugated polymers. Polym Chem. 2015;6:5036–9.
67. Lai YY, Tung TC, Liang WW, Cheng YJ. Synthesis of poly(3-hexylthiophene), poly(3-hexylselenophene), and poly(3-hexylselenophene-alt-3-hexylthiophene) by direct C–H arylation polymerization via *N*-heterocyclic carbene palladium catalysts. Macromolecules. 2015;48:2978–88.

Kazuhiro Nakabayashi received his B. S. degree from Nagoya Institute of Technology in 2006 and later earned his M. S. in 2008, and Ph.D. degrees in 2011 from Tokyo Institute of Technology under the supervision of Prof. Mitsuru Ueda. After earning his Ph.D. degree, he has worked in Yamagata University as an assistant professor. During 2014, he also joined Prof. Timothy M. Swager group in Massachusetts Institute of Technology as a visiting researcher. He received the Award for Encouragement of Research in Polymer Science, the Society of Polymer Science, Japan in 2017. His research focuses on the development of functional polymeric materials and exploring the methodology of polymer synthesis.