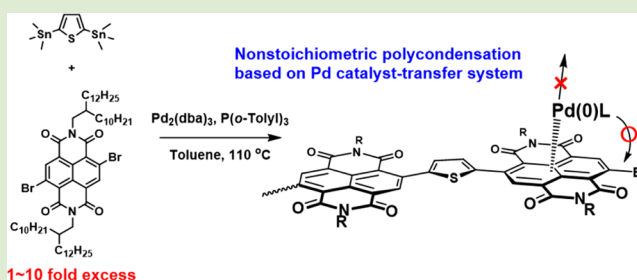


Nonstoichiometric Stille Coupling Polycondensation for Synthesizing Naphthalene-Diimide-Based π -Conjugated PolymersEisuke Goto,[†] Shinji Ando,[‡] Mitsuru Ueda,[†] and Tomoya Higashihara^{*,†}[†]Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan[‡]Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama 2-12-1-E4-5, Meguro-ku, Tokyo 152-8552, Japan

Supporting Information

ABSTRACT: A nonstoichiometric Stille coupling polycondensation was first succeeded between 2,5-bis-(trimethylstannyl)thiophene (1) and 4,9-dibromo-2,7-bis(2-decyltetradecyl)benzo[*lmn*][3,8]-phenanthroline-1,3,6,8-tetraone (2) with ratios ranging from 1:1 to 1:10. The model reaction using 2-(tributylstannyl)thiophene (3) and 4,9-dibromo-2,7-bis(2-hexyl)benzo[*lmn*][3,8]-phenanthroline-1,3,6,8-tetraone (4) at a 1:1 molar ratio in the presence of catalytic Pd₂(dba)₃/P(*o*-tolyl)₃ indicated that the rate constant of the second substitution reaction (k_2) is 15 times higher than that of the first one (k_1). It was found that the selective intramolecular catalyst transfer was promoted by the naphthalene-diimide (NDI) skeleton. The results also provided a new one-pot symmetrical end-functionalization method to synthesize an NDI-based n-type polymer with NDI groups at both α,ω -chain ends.



For the homogeneous polycondensation system using A2 and B2 type monomers, the number-average degree of polymerization (X_n) is expressed in an extension of Carother's equation^{1,2} as $X_n = (1 + r)/(1 + r - 2rp)$, where r is the stoichiometric ratio of reactants between the A2 and B2 type monomers and p is the extent of the reaction. Thus, the stoichiometry of the monomers is a crucial factor in obtaining a high-molecular-weight polymer. This classical theory is based on the assumption of the equal reactivity between the functional groups in the monomers.

Hill et al. reported the significant deviation from the classical theory for the synthesis of poly(*p*-phenylene sulfide), in which stoichiometric monomer ratios are unnecessary.³ Odian and co-workers investigated the kinetics of the polymerization with the change in reactivity of one functional group upon the reaction of the other and determined the time-dependent X_n values for various rate constant ratios ($\kappa = k_2/k_1$).⁴ Kihara et al. performed the nonstoichiometric polycondensation of 4,4'-isopropylidenediphenol with a 1.7-fold excess of 2,2-dichloro-1,3-benzodioxole to afford a high-molecular-weight polycarbonate with the number-average molecular weight (M_n) value of 120 000, although the theoretical maximum M_n was 693.⁵ This is because the intermediate obtained by the first reaction of the diphenol with dioxole is much more reactive than the initial dioxole toward the diphenol. Therefore, the phenol groups always exist at both chain ends of the generating polymers, suppressing the termination reaction with an excess amount of the dioxole. Hay and co-workers also reported the synthesis of high-molecular-weight polyformals by the nonstoichiometric

polycondensation between potassium bisphenolate with excess amounts of dibromomethane.⁶ Ueda and co-workers reported the synthesis of polythioether from 4,4'-thiobisbenzenethiol and dibromomethane under nonstoichiometric conditions.⁷ Recently, Kimura and co-workers established the synthesis of aromatic polyesters^{8,9} and polyimides¹⁰ by the nonstoichiometric polycondensation in heterogeneous phases based on the reaction-induced crystallization technique, which have been well-reviewed elsewhere.¹¹

The catalyst-transfer systems¹² have also been developed. Nomura and co-workers utilized the Pd(0)-catalyzed Tsuji–Trost allylation reactions to realize a nonstoichiometric polycondensation. In this polymerization, after the first reaction of the monomers, the Pd(0) catalyst intramolecularly transfers to the other reactive site to activate the second reaction.^{13,14}

Yokozawa and co-workers have recently established the catalyst-transfer condensation polymerization (CTCP) using Pd(0) catalysts.^{15–17} Indeed, a wide variety of well-defined π -conjugated polymers including polyfluorene,¹⁴ polyphenylene,¹⁶ polythiophene,¹⁷ poly(fluorene-*alt*-benzothiadiazole),¹⁸ and poly(phenyleneethynylene)¹⁹ could be obtained by the CTCP with ^tBu₃PPd(Ar)Br. In addition, they investigated the structural requirements for the Pd(0) catalyst transfer on a C=C double bond under Suzuki–Miyaura coupling reaction conditions and concluded that the ortho position of the C=C

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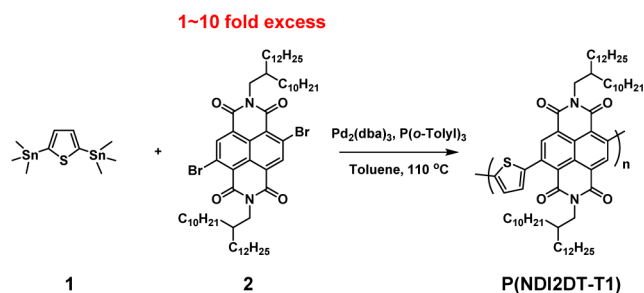
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C of stilbenes is critical for the selective intramolecular catalyst transfer.²⁰

On the other hand, representative n-type π -conjugated polymers, such as the naphthalene-diimide (NDI)-based polymers,^{21,22} showed an excellent organic field-effect transistor (OFET) electron mobility ($0.85\text{--}3.2\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$);^{23,24} therefore, their related materials have received special attention. Kiriy and co-workers investigated the chain-growth polycondensation of the NDI-based anion radical monomer in the presence of Ni(0)^{25,26} and Pd(0)^{27,28} catalysts. Therefore, the understanding of the catalyst-transfer systems during the synthesis of n-type π -conjugated polymers becomes highly important.

In the present study, we investigated the nonstoichiometric Stille coupling polycondensation between **1** and **2** with ratios ranging from 1:1 to 1:10 in the presence of Pd₂(dba)₃/P(*o*-tolyl)₃ (Scheme 1). The model reaction using **3** and **4** at a 1:1

Scheme 1. Nonstoichiometric Stille Coupling Polycondensation between **1** and **2**



molar ratio in the presence of a catalytic amount of Pd₂(dba)₃/P(*o*-tolyl)₃ indicated the rate constant ratio ($\kappa = 15$). Consequently, it was found that the presence of NDI moieties is critical for the selective intramolecular catalyst transfer. The most advantageous point of this nonstoichiometric polycondensation approach is that a new one-pot symmetrical end-functionalization method can be adopted to prepare an NDI-based n-type polymer with NDI groups at both of the α,ω -chain ends.

Table 1 shows the polymerization results for the various [2]₀/[1]₀ ratios. Under the conditions using excess amounts of **2**, the Stille coupling polycondensation proceeded to afford poly{[N,N'-bis(2-decyltetradecyl)-1,4,5,8-naphthalene diimide-2,6-diyl]-*alt*-thiophene-2,5-diyl} (P(NDI2DT-T1)) in almost quantitative yields based on the feeding quantity of **1**. Surprisingly, P(NDI2DT-T1) could be obtained even when

Table 1. Results of Nonstoichiometric Stille Coupling Polycondensation between **1 and **2**^a**

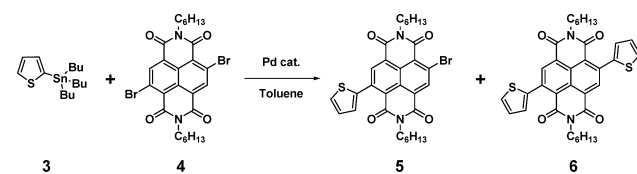
[2] ₀ /[1] ₀ ^b	M _n ^c	D ^c
0.5	- ^d	- ^d
1	23 500	2.00
1.25	17 800	1.93
2	14 500	1.64
4	10 200	1.46
10	8 500	1.42

^aThe polymerization yields were almost quantitative based on the feeding quantity of **1** when [2]₀/[1]₀ > 1. ^bThe feeding molar ratio of **2** and **1**. ^cDetermined by SEC in *o*-dichlorobenzene at 140 °C using polystyrene standards. ^dThe polymerization was not proceeded.

[2]₀/[1]₀ = 10, although the M_n values slightly decreased by increasing the [2]₀/[1]₀ ratio (see Figure S1). In sharp contrast, when a 2-fold excess of [1]₀ to [2]₀ was used ([2]₀/[1]₀ = 0.5), the polymerization did not occur at all. These results are quite reproducible by at least twice repeated experiments.

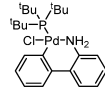
To understand in detail why high-M_n P(NDI2DT-T1) samples were obtained despite the highly asymmetric monomer feed ratio, we assume that the second reaction between the C–Br moiety of **2** and the trimethylstannyl moiety of **1** is much faster than the first one, so that the excess amount of **2** cannot participate in the termination at the generating polymer chain ends during the polymerization. To obtain evidence for this assumption, the 1:1 model reaction between **3** and an equivalent molar amount of **4** was investigated (see Scheme 2).

Scheme 2. 1:1 Model Reaction between **3** and **4**



In Table 2, the exclusive generation of the dicoupled product (**6**) was found in the absence of the monocoupled product (**5**),

Table 2. Results of 1:1 Model Reaction between **3 and **4**^a**

catalyst	yield (%) ^b	
	5	6
Pd ₂ (dba) ₃ , P(<i>o</i> -Tolyl) ₃	0	100
 Pd(PPh ₃) ₄	16	84

^aThe feeding molar ratio [4]₀/[3]₀ = 1. The model reactions were carried out in toluene at 90 °C for 2 h. ^bThe byproduct of unreacted **4** is excluded in the calculation.

when the Pd(0) catalysts, such as Pd₂(dba)₃/P(*o*-tolyl)₃ and chloro[(tri-*tert*-butylphosphine)-2-(2-aminobiphenyl)]-palladium(II), were used in the model reaction between **3** and **4**. The ¹H NMR spectra of the crude products obtained by the model reaction using Pd₂(dba)₃/P(*o*-tolyl)₃ are representatively shown in Figure 1. It is obvious that only **6** was obtained except for the residual **4** used in excess.

These results indicate that the second reaction between the C–Br moiety **4** and the tri-*n*-butylstannyl moiety of **3** is much faster than the first one. To further quantify the reaction rate constant ratio ($\kappa = k_2/k_1$), where k_1 and k_2 are the reaction rate constants for the first and second reaction steps, respectively, the kinetics was investigated in detail according to a previously reported method (see also Supporting Information).^{5,7} As a result, κ was determined to be 15, which means that the second reaction is 15 times faster than the first one.

On the basis of these findings, it is suggested that the Pd(0) catalysts intramolecularly transfer walking through the single molecule of **4** to obtain a high κ value (see Scheme S2). To check whether or not this catalyst-transfer system is specifically affected by the NDI skeleton, we further performed the model reactions between **3** and 1,4-dibromobenzene (**7**) or 2,6-

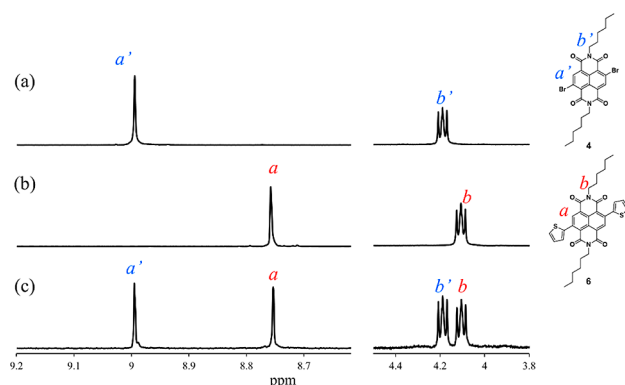
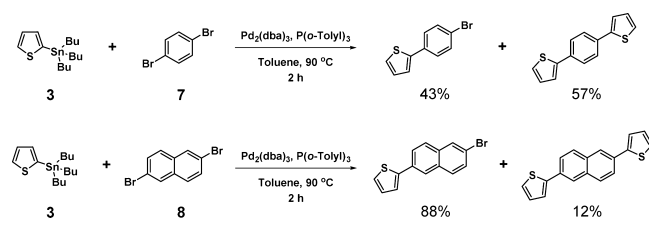


Figure 1. ^1H NMR spectra of (a) **4**, (b) **6**, and (c) the crude products obtained by the model reaction of **3** and **4** in toluene at 90°C for 2 h.

dibromonaphthalene (**8**), which possess a phenylene or naphthalene skeleton without the *N*-alkylated diimide moieties (see Scheme 3).

Scheme 3. 1:1 Model Reactions between **3** and **7/8**



In both cases, a significant amount of monocoupled products was obtained as can be seen in Scheme 3. Therefore, it can be concluded that for the nonstoichiometric Stille coupling polycondensation between **1** and **2** the Pd(0) catalyst intramolecularly transfers through a single molecule of **2** specifically assisted by the NDI skeleton.

Finally, we extended this nonstoichiometric Stille coupling polycondensation to synthesize poly{[*N,N'*-bis(2-decyltetradecyl)-1,4,5,8-naphthalene diimide-2,6-diyl]-*alt*-(2,2'-bithiophene)-5,5'-diyl} (P(NDI2DT-T2)) using 5,5'-di(trimethylstannyl)-2,2'-bithiophene (**9**) instead of **1** in order to generalize this system (see Scheme S1). Indeed, the high-molecular-weight P(NDI2DT-T2) ($M_n = 22\,600$, $\bar{D} = 2.98$) was obtained by the Stille coupling polycondensation of **9** and a 2-fold excess of **2** in the presence of a catalytic amount of $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tolyl})_3$.

The ^1H NMR spectrum of P(NDI2DT-T2) ($[\text{2}]_0/[\text{9}]_0 = 2$, see Figure S3) shows typical resonance signals assignable to the main chain (see signals 1–6 in Figure S3). Besides, only the signals are observed assignable to the terminal NDI units of P(NDI2DT-T2) (8.86 and 8.81 ppm for H-terminated NDI (see signals 2a and 2b, respectively)).²⁴ There are no signals corresponding to the thiophene terminal units at all. Therefore, it was concluded that the NDI units were finally introduced at both α,ω -chain ends after the polymerization in an almost quantitative yield. It should be noted that Br-terminated NDI was not found around ~ 9.0 ppm.²⁴ The oxidatively inserted Pd species within the terminal NDI–Br bond probably lead to the dehalogenation by quenching the polymerization with HCl. The existence of intermediate terminal NDI–Pd–Br implies that the rate-determining step is transmetalation.

In conclusion, the nonstoichiometric Stille coupling polycondensation of **1** and **2** catalyzed by $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tolyl})_3$ was first discovered in which P(NDI2DT-T1) was successfully obtained by employing the monomer feed ratio ($[\text{2}]_0/[\text{1}]_0$) in the range of 1–10. The nonstoichiometric Stille coupling polycondensation of **9** with a 2-fold excess of **2** could also be performed to afford the high-molecular-weight P(NDI2DT-T2). The kinetics of the model reaction between **3** and **4** showed the high κ value of 15. On the basis of the results of the detailed model reactions of **3** with **7** or **8**, it was found that the NDI skeleton is crucial for the selective intramolecular catalyst-transfer system. Such a nonstoichiometric polycondensation approach provides the new one-pot symmetrical end-functionalization method to succeed in synthesizing an α,ω -difunctional NDI-based n-type polymer at both chain ends. The investigation of the chain-growth Stille coupling polycondensation of NDI-containing monomers by exploiting this catalyst-transfer system is now also ongoing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00532.

Detailed experimental procedures, characterization of compounds for model reactions and polymerization, UV–vis and NMR spectra, and the calculation for the reaction rate constant (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
- (2) Odian, G. *Principle of Polymerization*, 3rd ed; Wiley: New York, 1991; Chapter 2.
- (3) Hill, H.; Wayne, Jr.; Edmonds, J. T., Jr. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1972**, *13* (1), 603.
- (4) Ozizmir, E.; Odian, G. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1089–1097.
- (5) Kihara, N.; Komatsu, S.; Takata, T.; Endo, T. *Macromolecules* **1999**, *32*, 4776–4783.
- (6) Miyatake, K.; Hill, A. R.; Hay, A. S. *Macromolecules* **2001**, *34*, 4288–4290.
- (7) Iimori, H.; Shibasaki, Y.; Ando, S.; Ueda, M. *Macromol. Symp.* **2003**, *199*, 23–36.
- (8) Kimura, K.; Kohama, S.; Yamashita, Y. *Macromolecules* **2002**, *35*, 7545–7552.

- (9) Kohama, S.; Kimura, K.; Yamashita, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1757–1766.
- (10) Wakabayashi, K.; Kohama, S.; Yamazaki, S.; Kimura, K. *Macromolecules* **2008**, *41*, 1168–1174.
- (11) Kimura, K. In *Nonstoichiometric Polycondensation*, Polymer Science: A Comprehensive Reference; Matyjaszewski, K., Moler, M., Schmidt, H. W., Ueda, M. Elsevier: Amsterdam, 2012; Vol. 5, pp 95–112.
- (12) Kiriy, A.; Senkovskyy, V.; Sommer, M. *Macromol. Rapid Commun.* **2011**, *32*, 1503–1517.
- (13) Nomura, N.; Tsurugi, K.; Okada, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1932–1935.
- (14) Nomura, N.; Tsurugi, K.; RajanBabu, T. V.; Kondo, T. *J. Am. Chem. Soc.* **2004**, *126*, 5354–5355.
- (15) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237.
- (16) Yokozawa, T.; Kohno, H.; Ohta, Y.; Yokoyama, A. *Macromolecules* **2010**, *43*, 7095–7100.
- (17) Yokozawa, T.; Suzuki, R.; Nojima, M.; Ohta, Y.; Yokoyama, A. *Macromol. Rapid Commun.* **2011**, *32*, 801–806.
- (18) Elmalem, E.; Kiriy, A.; Huck, W. T. S. *Macromolecules* **2011**, *44*, 9057–9061.
- (19) Kang, S.; Ono, R. J.; Bielawski, C. W. *J. Am. Chem. Soc.* **2013**, *135*, 4984–4987.
- (20) Nojima, M.; Ohta, Y.; Yokozawa, T. *J. Am. Chem. Soc.* **2015**, *137*, 5682–5685.
- (21) Guo, X.; Watson, M. D. *Org. Lett.* **2008**, *10*, 5333–5336.
- (22) Sommer, M. *J. Mater. Chem. C* **2014**, *2*, 3088–3098.
- (23) Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dötz, F.; Kastler, M.; Facchetti, A. *Nature* **2009**, *457*, 679–686.
- (24) Matsidik, R.; Komber, H.; Luzio, A.; Caironi, M.; Sommer, M. *J. Am. Chem. Soc.* **2015**, *137*, 6705–6711.
- (25) Senkovskyy, V.; Tkachov, R.; Komber, H.; Sommer, M.; Heuken, M.; Voit, B.; Huck, W. T. S.; Kataev, V.; Petr, A.; Kiriy, A. *J. Am. Chem. Soc.* **2011**, *133*, 19966–19970.
- (26) Senkovskyy, V.; Tkachov, R.; Komber, H.; John, A.; Sommer, J. U.; Kiriy, A. *Macromolecules* **2012**, *45*, 7770–7777.
- (27) Tkachov, R.; Karpov, Y.; Senkovskyy, V.; Raguzin, I.; Zessin, J.; Lederer, A.; Stamm, M.; Voit, B.; Beryozkina, T.; Bakulev, V.; Zhao, W.; Facchetti, A.; Kiriy, A. *Macromolecules* **2014**, *47*, 3845–3851.
- (28) Tkachov, R.; Komber, H.; Rauch, S.; Lederer, A.; Oertel, U.; Häußler, L.; Voit, B.; Kiriy, A. *Macromolecules* **2014**, *47*, 4994–5001.