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Fast Controlled Living Polymerization of Arylisocyanide Initiated by Aromatic Nucleophile Adduct of Nickel Isocyanide Complex

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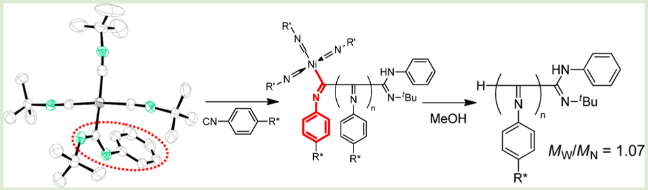
Supporting Information



ABSTRACT: The fast living polymerization of chiral arylisocyanide in the presence of the aromatic nucleophile adduct of tetra(t-butylisocyano)nickel(II) complex as an initiator gave the predominantly one-handed helical polyisocyanide with narrow polydispersity. X-ray crystal structures of initiators and MALDI-TOF MS and NMR studies of the polymer products elucidated the key role of the aromatic substituents in the initiator and monomer achieving narrow polydispersity. The aromatic groups in the initiator and monomer stabilized the electronic structure of the carbene-like ligand to suppress dissociation of the active nickel complex that leads to chain transfer and termination. The aromatic groups also controlled the reactivity of the active site for initiation and propagation.

Living polymerization methods allow a wide variety of polymer shapes, such as block copolymers, graft polymers, and star-shaped polymers, which enable access to various kinds of self-assembled, supramolecular architectures with defined shapes and properties. Since the discovery of living anionic polymerization by Szwarc et al. in 1956,[1] many kinds of living polymerization methods have been developed, mainly in addition polymerization of vinyl monomers and ring-opening polymerization of cyclic monomers. These methods have allowed the synthesis of polymers with controllable molecular weights and narrow molecular weight distributions. Although π-conjugated polymers have attracted much attention as active components of thin-film solar cells,[2] light-emitting diodes,[3] field-effect transistors,[4] and electrical semiconductors,[5] the use of living polymerization methods to give π-conjugated polymers with nominated molecular weights and narrow polydispersities has been rare before this decade.[6] Since the chain-growth synthesis of poly(3-hexylthiophene) from Ni-catalyzed cross-coupling reactions was reported by Yokozawa et al.[7] and McCullough et al.[8] in 2004, controlled living polymerization methods have emerged for a variety of π-conjugated polymers, including polyfluorene,[9] poly(p-phenylene),[10] and polycarbazole,[9b] and have enabled the preparation of various kinds of their block copolymers.[11]

Polyisocyanides have a unique π-conjugation system with C=N double bonds at the carbons that connect the monomer units, which twist along the polymer backbone to create a helical conformation. Although living polymerizations of isocyanide have been achieved by using η^3-allyl nickel catalyst,[12] aryl rhodium complex,[13] μ-ethynediyl Pt−Pd binuclear complex,[14] or nickel complex at the end of polythiophene[15] as initiators, their successful application in block copolymer synthesis or surface graft polymerization has been difficult because of their narrow tolerance to initiator and terminator structures and polymerization conditions. Nolte et al. have thoroughly studied the polymerization of aliphatic isocyanides using the amine adduct of tetra(t-butylisocyano)nickel(II) complex as the initiator under aerated atmosphere[16] and have developed a convenient route for block copolymer synthesis[17] and surface graft polymerization[18] by using amino-functionalized macroinitiator and monolayer, respectively. However, their polymerizations were not fully controlled and the reported polydispersities were larger than that in the above-mentioned cases of living polymerization. According to the proposed "merry-go-round polymerization" mechanism,[12a,16b,d] the active site in the initiator and the propagation terminal is supposed to be a nickel complex that is tetracoordinated with three isocyano ligands and a carbene-like ligand.[16c,e] In general, a living polymerization can be attained when the propagating polymer chains undergo neither chain transfer nor termination, and the molecular weight distribution usually becomes narrow when the initiation rate is sufficiently higher than the propagation rate. In this study, we propose a fast controlled living polymerization system for aromatic isocyanides by tuning the stability and reactivity of the terminal nickel complex through the electronic

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Scheme 1. Polymerization of Isocyanide Initiated by Nucleophile Adduct of Tetra(*t*-butylisocyano)nickel(II) Complex

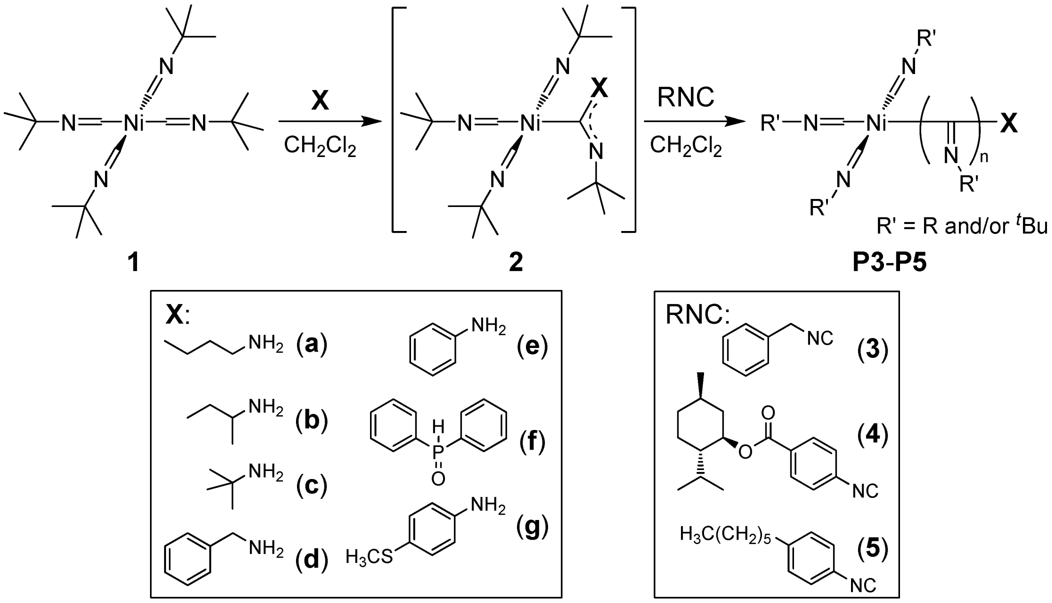

Table 1. Polymerization of Isocyanide Initiated by Various Nucleophile Adducts of Tetra(*t*-butylisocyano)nickel(II) Complex[a]

entry	initiator	monomer	temp (°C)	$[M]_0$ (mM)	$[M]_0/[I]_0$	M_n[b]	PDI[b]
1	**2d**	**3**	r.t.	400	70	2180	40
2	**2a**	**4**	r.t.	450	40	3370	1.51
3	**2b**	**4**	r.t.	450	40	4130	1.47
4	**2c**	**4**	r.t.	450	40	11500	1.48
5	**2d**	**4**	r.t.	400	70	14800	1.23
6	**2e**	**4**	r.t.	430	71	7600	1.07
7			r.t.	43	70	9720	1.10
8			r.t.	8.5	70	15500	1.26
9			0[c]	440	70	7400	1.11
10		**5**	r.t.[d]	400	70	2700	1.79
11	**2f**	**4**	r.t.	450	80	11900	1.21
12			r.t.	43	70	14000	1.17
13	**2g**	**4**	r.t.	450	80	9600	1.11
14	Pt–Pd[e]	**4**	65[f]	440	83	11800	1.14

[a] Polymerization carried out in aerated dichloromethane for 30 min when the monomer was already completely consumed. [b] Estimated by GPC based on polystyrene standards. [c] Polymerization time was 1 h. [d] 55% of monomer remained. [e] *μ*-Ethynediyl Pt–Pd binuclear complex. [f] Polymerization was carried out in THF under argon for 24 h.

structure and steric hindrance of the substituents on the carbene-like ligand.

According to the procedure reported by Nolte et al.,[16] the initiators **2** were prepared by the treatment of tetra(*t*-butylisocyano)nickel(II) perchlorate **1** with amines **a**–**e** or diphenylphosphine oxide **f** (Scheme 1). The formation of the initiator complexes were confirmed from the shifts of the N≡C stretching band on Fourier transform infrared (FT-IR) spectra. Polymerizations were carried out in aerated dichloromethane at room temperature. The monomers were completely consumed to give the corresponding polymers within a few minutes. The number-averaged molecular weight (M_n) together with the polydispersity (PDI = M_w/M_n) of products, after sufficient time to consume the monomers, are summarized in Table 1. The polymerization of aliphatic monomer **3** initiated by aniline adduct **2e** gave a product with a broad polydispersity and a high yield of low molecular weight material (entry 1). However, the polymerization of aromatic monomer tethered by electron-withdrawing group **4** afforded a well-defined polyisocyanide with a very narrow polydispersity of 1.07 and no oligomeric products (entry 6). The polymerization of **4** initiated by **2e** under dilute conditions (entry 7) or with the reaction temperature lowered to 0 °C (entry 9) gave **P4e** with a low polydispersity of less than 1.11 at a moderate polymerization rate that consumed the monomer within 30 min. In contrast, the polymerizations of monomer **4** using the aliphatic amine adducts **2a**–**c** as initiators gave products showing multimodal gel permeation chromatography (GPC) profiles and containing low molecular weight fractions (entries 2–4). Benzylamine adduct **2d** afforded **P4d** with a smaller oligomer fraction than observed for **2a**–**c**, but the polydispersity was still higher than that of **P4e** (entry 5). The aromatic substituents of both monomer and amine, which are directly conjugated with the polymer main chain, should therefore play an important role in controlling the polymerization of isocyanide with a narrow polydispersity. In this context, the diphenylphosphine oxide adduct **2f** was also examined as an initiator, and it was found to afford the unimodal products with relatively narrow poly-

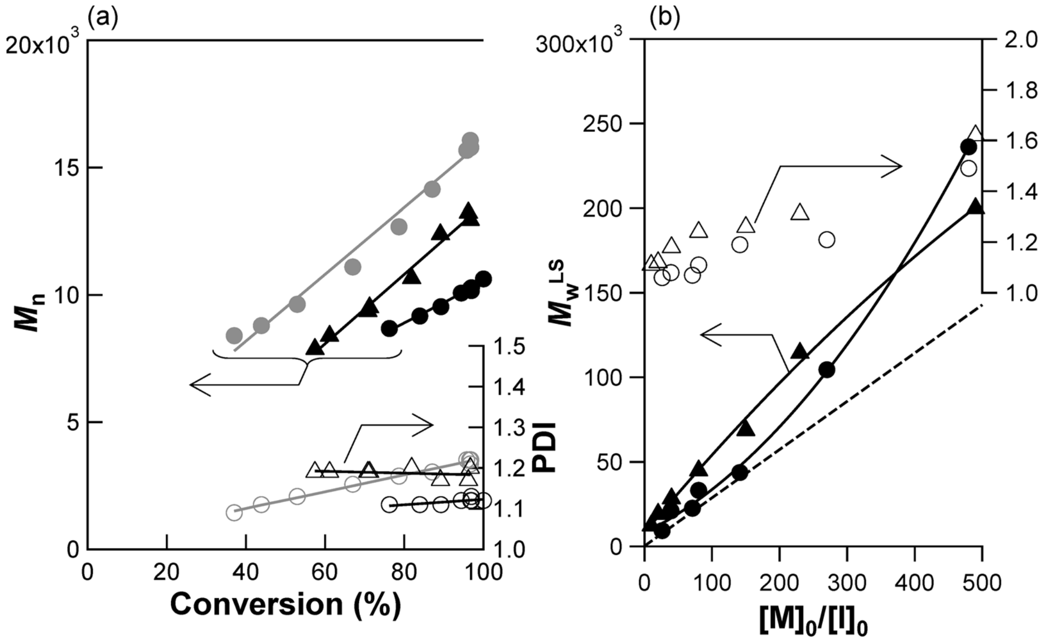

Figure 1. Averaged molecular weights (closed) and polydispersities (open marks) of poly(arylisocyanide)s **P4e** (circles) and **P4f** (triangles). (a) Number-averaged molecular weights based on polystyrene standards plotted against monomer conversion upon polymerization at $[M]_0$ of 43 (black) or 8.5 mM (gray). The pseudo first-order kinetic plots at the initial stage of polymerization are shown as the inset. (b) Averaged absolute molecular weight plotted the molar ratio of monomer to initiator. Theoretical value is shown with the broken line.

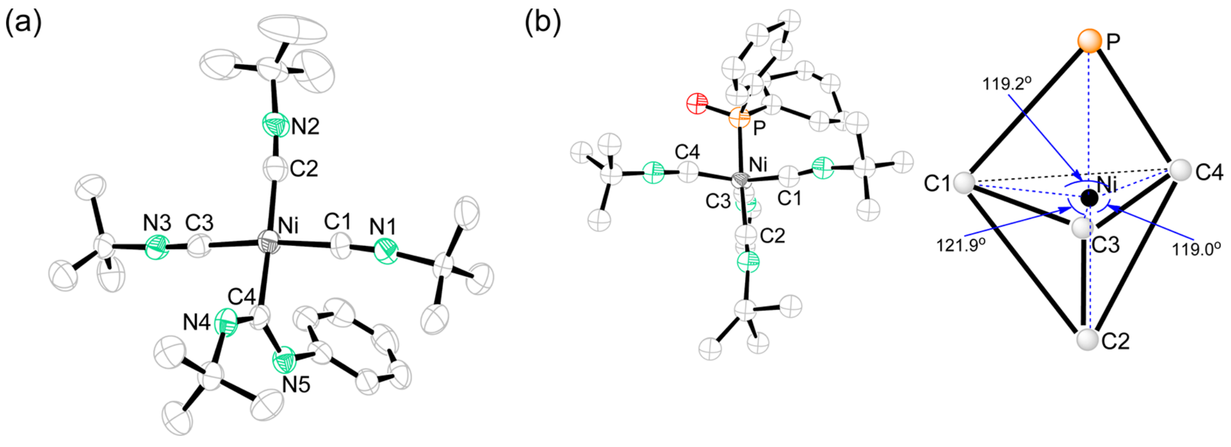

Figure 2. (a) ORTEP drawing of the crystallographically determined structure of **2e**. Selected bond lengths (Å) and angles (deg): Ni–C1, 1.854(6); Ni–C2, 1.876(7); Ni–C3, 1.848(6); Ni–C4, 1.912(6); C1–N1, 1.145(8); C2–N2, 1.139(9); C3–N3, 1.153(8); C4–N4, 1.319(8); C4–N5, 1.334(7); C1–Ni–C2, 90.5(3); C1–Ni–C3, 174.4(3); C2–Ni–C4, 176.2(3); Ni–C4–N4, 114.6(4); Ni–C4–N5, 122.5(4); N4–C4–N5, 122.9(5). (b) Crystal structure (left) and coordination environment (right) of **2f**.

dispersities of less than 1.21 (entry 11), even under dilute conditions (entry 12). The living nature of the polymerization of **4** with **2e** was confirmed by the multistep feeding of monomer (see Supporting Information).

The polymerization of **4** with **2e** was so fast that the monomer was completely consumed within 1 min. To analyze the polymerization kinetics, the polymerization was conducted under dilute conditions. As shown in Figure 1a, the M_n values increased in proportion to the conversion, and the monomer was consumed in accordance with pseudo-first-order kinetics. While the polydispersities were slightly decreased down to 1.10 at the monomer concentration of 43 mM (entry 6), they were slightly increased up to 1.26 at the dilute condition of 8.5 mM (entry 8). This suggests that the lower limit of monomer concentration to retain the controlled living polymerization condition should exist in the range of 10–40 mM. The polymerization of aromatic isocyanide with an electron-donating alkyl group (**5**) was not complete within 30 min, even at the high monomer concentration of 400 mM. The reaction was much slower than the reaction of **4** under extremely dilute conditions and gave **P5e** with a high polydispersity of 1.79 (entry 10).

The polymerization was also conducted with various feed ratios of monomer (**4**) to initiator (**2e**). The absolute molecular weights (M_w^{LS}) of the obtained polymers **P4e** determined by gel permeation chromatography–multiangle light scattering (GPC–MALS) analyses showed good agreement with the theoretical averaged molecular weights calculated from monomer/initiator ratios below 150 with narrow polydispersities of less than 1.20 (Figure 1b). For the polymerization of **4** initiated by **2f** (entries 11 and 12), the M_n value increased in proportion to the conversion and retained a polydispersity near

1.20, but the polymerization rate was considerably slower than the reaction initiated by **2e** under the same conditions (entry 7). The M_w^{LS} values of **P4f** were slightly larger than the corresponding theoretical values, implying that the initiator efficiency and the rate of initiation by **2f** should be lower than for **2e**. This is also supported by the fact that the molar mass of the polymer fraction of **P4e** on the GPC-MALS profile was almost constant, while that of **P4f** was slightly decreased by elution volume (see Supporting Information).

To investigate the difference in the initiation process, single crystals of **2e** and **2f** were prepared for X-ray diffraction analysis. The polymerizations using these crystalline forms were confirmed to give the same results as the reactions with the amorphous forms of **2e** and **2f**. In the case of **2e**, a *t*-butylisocyano ligand undergoes nucleophilic attack by the aniline amino group at the isocyano carbon to form a carbene-like ligand, which coordinates to the nickel center in the square planar conformation together with the three other *t*-butylisocyano ligands, as shown in Figure 2a. The N−C−N plane of the carbene ligand is near orthogonal to the square plane through the nickel and the other three isocyano ligands. The distances between the coordinating carbon and the two nitrogen atoms in the carbene ligand are comparable (1.32 and 1.33 Å), implying that the electrons in the carbene moiety are delocalized. A similar crystal structure for a benzylamine adduct to tetra(*t*-pentylisocyano)nickel(II) complex has been already reported by Nolte et al.,[16e] but the distance between the coordinating carbon and a nitrogen derived from the isocyanide (1.22 Å) was shorter than that from the amine (1.35 Å) in the carbene ligand. This suggests that the former N−C bond has double-bond character and therefore the electrons are not fully delocalized over the N−C−N group. The aniline-derived phenyl group directly conjugated with the carbene group in **2e** should play an important role in stabilizing the electronic structure of the carbene ligand. Although the crystal structure of **2f** suffered from disorder, especially at the aromatic rings of the phosphine oxide, the nickel center was elucidated to be pentacoordinated by four *t*-butylisocyano ligands and a phosphine oxide in a trigonal bipyramidal conformation (Figure 2b). The phosphine, nickel center, and an isocyano ligand are almost in a line to form a unique axis, which is almost perpendicular to the equatorial plane defined by the three other isocyano ligands. The pioneering study of the merry-go-round polymerization mechanism of isocyanide by Nolte et al. proposed the formation of a pentacoordinated nickel complex that preceded reorganization to the square planar complex[12a,16b,d] without any experimental evidence. The axial phosphine oxide ligand reacts with one of the isocyano ligands to form a carbene-like ligand before the initiation of polymerization, which should cause some delay of initiation and decrease the initiator efficiency and rate of initiation.

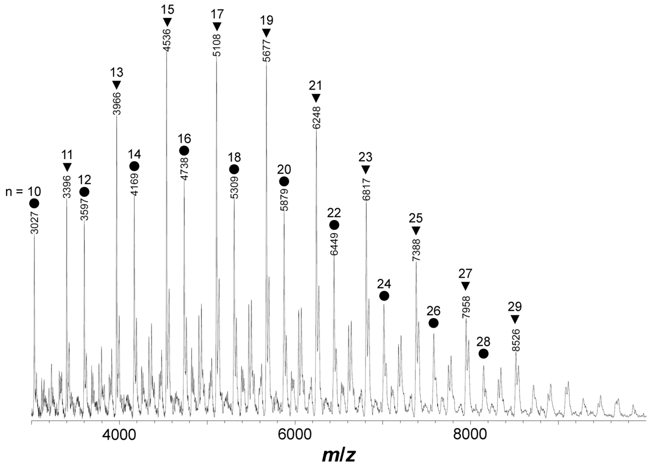

Figure 3. MALDI-TOF mass spectrum of **P4e**. Number of repeat unit (n) is denoted on each peak. Two series of peaks marked with circles or triangles can be assigned as the polymer fractions having one or two *t*-butylisocyanide units, respectively.

The detailed structures of the obtained polyisocyanides **P4e** and **P4f** were analyzed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. As shown in Figure 3, the spectrum of **P4e** is mainly composed of two series of peaks; one series (indicated by circles) can be expressed as 285.17n (repeat unit) + 1.01 (H) + 92.05 (aniline − H) + 83.07 (*t*-butylisocyanide), while the other (triangles) can be expressed as 285.17n + 1.01 + 92.05 + 83.07 × 2, where n is the number of repeat units. Thus, one or two *t*-butylisocyano ligands were supposed to be incorporated in the polymer chain. One *t*-butylisocyano ligand reacts with aniline to form a carbene-like active site upon initiator preparation, while another one should be accommodated into the polymer chain, competing with the aromatic isocyanide monomers **4** in the course of polymerization. Peaks that could be assigned to the polymer with the nickel complex were not observed, suggesting that the active site should be quenched by reprecipitation in methanol and that the nickel complex was removed from the polymer terminal and substituted with a proton. The mass spectrum for **P4f** was also mainly composed of two series of peaks expressed as the analogous equations changed by replacing aniline (92.05) with a phosphine oxide end group (201.05), as shown in Supporting Information. The propagation mechanism is therefore independent of the initiator structure. In the ^{31}P NMR spectra, the phosphine in the initiator **2f** showed a peak at 114 ppm, which was at a considerably lower field than the phosphine oxide (22 ppm) and demonstrates the effect of coordination to the nickel center. After removal of the nickel complex by reprecipitation in methanol, the isolated polymer gave a ^{31}P peak at 19 ppm, which is comparable to the phosphine oxide. The polymerization was conducted in the NMR tube at the diluted condition ([initiator] = 3.6 mM, [monomer] = 18 mM) in $CDCl_3$ at −10 °C. Upon polymerization, a broad peak assigned as the carbene-like complex emerged at 80 ppm, after which a set of sharp peaks for the oligomeric-to-polymeric products was observed in the high field region while the peak intensity of the initiator was slightly decreased. The emergence of peaks at high field reflects the increased average distance between the phosphine and the metal center as the polymerization proceeds, supporting the proposed merry-go-round mechanism based on the insertion of monomers between the carbene ligand and the nickel center.[12a,16b,d]

Polyisocyanides are thought to have a stable 4_1 helical conformation in solution, according to data from circular dichroic (CD) spectra[19] and from molecular modeling calculations in combination with NMR studies.[20] The μ-ethynediyl Pt−Pd binuclear complex has been reported by Takahashi et al. to give poly(arylisocyanide) with well-defined one-handed helical conformation,[14b,c,h] which was directly observed on highly oriented pyrolytic graphite at a molecular resolution by atomic force microscopy.[14a,21] The UV−vis spectra of **P4e** and **P4f** exhibited the typical absorption band attributable to the conjugated imino groups in the main chain with slightly larger absorption coefficients than that of **P4h** prepared by using the μ-ethynediyl Pt–Pd binuclear complex, as shown in Figure 4. The absorption shoulders of **P4e** and **P4f** extended up to 700 nm, while that of **P4h** extended to about 560 nm. These polymers also showed the strong circular dichroism in the main chain absorption region: the positive Cotton effect was observed in the range of 300–500 nm. The $\Delta\varepsilon$ values of **P4e** and **P4f** were comparable to each other but smaller than that of **P4h**, suggesting that the polymers synthesized by using nickel complexes have some disorder in the helical conformation, which comes from the disarray in the side chains. Although the side chains are unidirectionally arranged in the ideal helical structure, some of them should be disarranged to give the s-*trans* form because of steric repulsion between the side chains and where the orbital overlap between the imino groups is enhanced to extend the absorption shoulder toward longer wavelength.

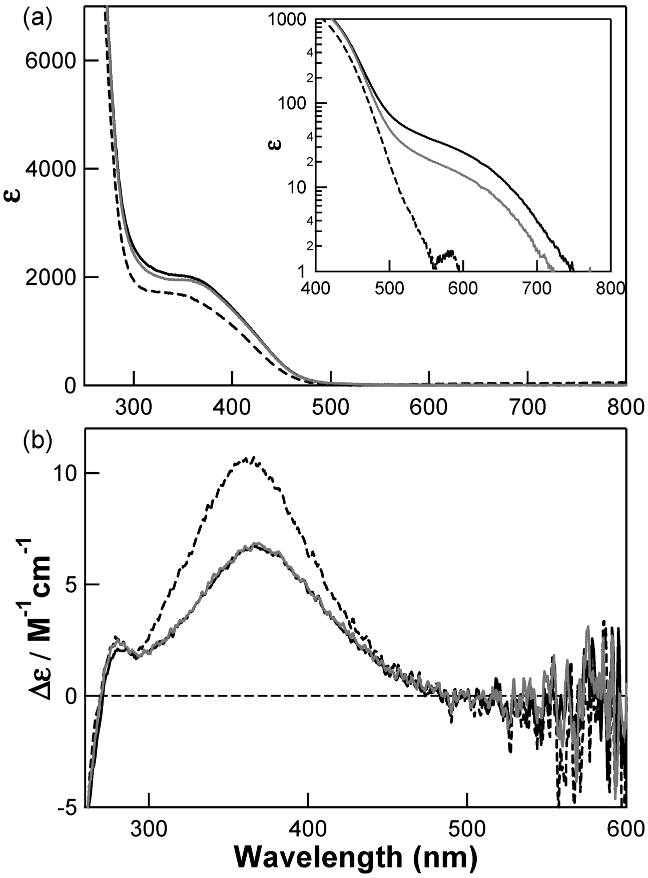

Figure 4. UV–vis (a) and CD (b) spectra of **P4e** (black full line) and **P4f** (gray full line) as a comparison with those of **P4h** (broken line) prepared by using μ-ethynediyl Pt–Pd complex. UV–vis spectra are shown with logarithmic scale on the inset of (a) to enlarge the absorption shoulder region.

In conclusion, we have demonstrated the fast controlled living polymerization of isocyanide by using aromatic isocyanide and the aromatic nucleophile adduct of tetra(*t*-butylisocyano)nickel(II) complex as monomer and initiator, respectively. The aromatic groups in the initiator and monomer stabilize the electronic structure of the carbene-like ligand to suppress dissociation of the active nickel complex, leading to less chain transfer and/or termination, and also influence the reactivity of the active site for initiation and propagation. This controlled living polymerization can be conducted at ambient temperature under an aerated atmosphere, and the modification of the nucleophile structure, which is regiospecifically incorporated at the end of polymer backbone, also allows the preparation of various block copolymers and graft polymers. This versatility of this polymerization should allow the fabrication of various molecular devices based on the unique π-conjugation system of polyisocyanides.

Given that the film of poly(α-methylheptylisocyanide) is reported to exhibit weak conductivity,[22] our living polymerization method for arylisocyanides could be applied for investigation of single-molecular wires with moderate charge transport rates. As shown in Table 1, the initiator **2g**, which was prepared by treatment with 4-methylthioaniline, also gave the poly(arylisocyanide) **P4g** with a narrow polydispersity of 1.11, suggesting that the sulfur-containing functional group does not affect the living polymerization mechanism (entry 13). Based on this result, the controlled surface graft polymerization from a gold surface modified by 4-aminothiophenol is now under investigation. We have already examined the use of various terminators, including terpyridine-type ligands, which unfortunately could not completely terminate the polymerization but rather reduced the reaction rate. The use of effective terminators that are indispensable in establishing molecular wiring is now also under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Procedures for preparation of monomer **4** and initiator adducts **2a–g**; GPC profiles of unpurified polymers; GPC-MALS profiles of **P4e** and **P4f**; result of polymerization through multistep momomer feeding; X-ray crystal data and structure refinement for **2e** and **2f**; MALDI-TOF mass spectrum of **P4f**; ^{31}P NMR spectra of **P4f** during polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656.

(2) (a) Beaujuge, P. M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2011**, *133*, 20009. (b) Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323. (c) Hoppe, H.; Sariciftci, N. S. In *Photoresponsive Polymers II*; Marder, S. R., Lee, K. S., Eds.; Springer-Verlag: Berlin, Germany, 2008; Vol. *214*, p 1.

(3) (a) Grimsdale, A. C.; Leok Chan, K.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897. (b) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281. (c) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A. D.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(4) (a) Sirringhaus, H.; Bird, M.; Zhao, N. *Adv. Mater.* **2010**, *22*, 3893. (b) Tessler, N.; Veres, J.; Globerman, O.; Rappaport, N.; Preezant, Y.; Roichman, Y.; Solomesch, O.; Tal, S.; Gershman, E.;

Adler, M.; Zolotarev, V.; Gorelik, V.; Eichen, Y. *Handbook of Conducting Polymers*, 3rd ed.; CRC Press: Boca Raton, FL, 2007; Vol. 2, p 7/1; (c) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365.

(5) (a) Heeger, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2591. (b) MacDiarmid, A. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2581. (c) Shirakawa, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2574.

(6) (a) Masuda, T.; Sanda, F. *Handbook of Metathesis*; Wiley-VCH Verlag GmbH: Germany, 2008; p 375; (b) Mayershofer, M. G.; Nuyken, O. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5723.

(7) (a) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromol. Rapid Commun.* **2004**, *25*, 1663. (b) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169. (c) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542.

(8) (a) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526. (b) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649.

(9) (a) Huang, L.; Wu, S.; Qu, Y.; Geng, Y.; Wang, F. *Macromolecules* **2008**, *41*, 8944. (b) Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D. *Macromolecules* **2008**, *42*, 30. (c) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236.

(10) Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2006**, *128*, 16012.

(11) (a) Jeffries-El, M.; Sauvé, G.; McCullough, R. D. *Adv. Mater.* **2004**, *16*, 1017. (b) Botiz, I.; Darling, S. B. *Macromolecules* **2009**, *42*, 8211. (c) Iovu, M. C.; Jeffries-El, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. *Polymer* **2005**, *46*, 8582. (d) Urien, M.; Erothu, H.; Cloutet, E.; Hiorns, R. C.; Vignau, L.; Cramail, H. *Macromolecules* **2008**, *41*, 7033. (e) Ouhib, F.; Khoukh, A.; Ledeuil, J.-B.; Martinez, H.; Desbriéres, J.; Dagron-Lartigau, C. *Macromolecules* **2008**, *41*, 9736. (f) Ohshimizu, K.; Ueda, M. *Macromolecules* **2008**, *41*, 5289. (g) Zhang, Y.; Tajima, K.; Hirota, K.; Hashimoto, K. *J. Am. Chem. Soc.* **2008**, *130*, 7812. (h) Wu, P.-T.; Ren, G.; Li, C.; Mezzenga, R.; Jenekhe, S. A. *Macromolecules* **2009**, *42*, 2317. (i) Park, S.-J.; Kang, S.-G.; Fryd, M.; Saven, J. G.; Park, S.-J. *J. Am. Chem. Soc.* **2010**, *132*, 9931. (j) Lee, E.; Hammer, B.; Kim, J.-K.; Page, Z.; Emrick, T.; Hayward, R. C. *J. Am. Chem. Soc.* **2011**, *133*, 10390. (k) Ho, V.; Boudouris, B. W.; McCulloch, B. L.; Shuttle, C. G.; Burkhardt, M.; Chabinyc, M. L.; Segalman, R. A. *J. Am. Chem. Soc.* **2011**, *133*, 9270.

(12) (a) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9101. (b) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 7926. (c) Deming, T. J.; Novak, B. M. *Macromolecules* **1991**, *24*, 326.

(13) (a) Onitsuka, K.; Mori, T.; Yamamoto, M.; Takei, F.; Takahashi, S. *Macromolecules* **2006**, *39*, 7224. (b) Onitsuka, K.; Yamamoto, M.; Mori, T.; Takei, F.; Takahashi, S. *Organometallics* **2006**, *25*, 1270. (c) Yamamoto, M.; Onitsuka, K.; Takahashi, S. *Organometallics* **2000**, *19*, 4669.

(14) (a) Wu, Z.-Q.; Nagai, K.; Banno, M.; Okoshi, K.; Onitsuka, K.; Yashima, E. *J. Am. Chem. Soc.* **2009**, *131*, 6708. (b) Takei, F.; Onitsuka, K.; Takahashi, S.; Terao, K.; Sato, T. *Macromolecules* **2007**, *40*, 5245. (c) Takei, F.; Onitsuka, K.; Takahashi, S. *Macromolecules* **2005**, *38*, 1513. (d) Onitsuka, K.; Yabe, K.-I.; Ohshiro, N.; Shimizu, A.; Okumura, R.; Takei, F.; Takahashi, S. *Macromolecules* **2004**, *37*, 8204. (e) Takei, F.; Nakamura, S.; Onitsuka, K.; Ishida, A.; Tojo, S.; Majima, T.; Takahashi, S. *Chem. Lett.* **2003**, *32*, 506. (f) Hida, N.; Takei, F.; Onitsuka, K.; Shiga, K.; Asaoka, S.; Iyoda, T.; Takahashi, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 4349. (g) Takei, F.; Hayashi, H.; Onitsuka, K.; Kobayashi, N.; Takahashi, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 4092. (h) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Chem.—Eur. J.* **2000**, *6*, 983.

(15) Wu, Z.-Q.; Ono, R. J.; Chen, Z.; Bielawski, C. W. *J. Am. Chem. Soc.* **2010**, *132*, 14000.

(16) (a) Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. *J. Chem. Soc., Chem. Commun.* **1986**, 1789. (b) Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 6818. (c) Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 175. (d) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039. (e) Metselaar, G. A.; Schwartz, E.; de Gelder, R.; Feiters, M. C.; Nikitenko, S.; Smolentsev, G.; Yalovega, G. E.; Soldatov, A. V.; Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M. *ChemPhysChem* **2007**, *8*, 1850.

(17) (a) Cornelissen, J. J. L. M.; Fischer, M.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *Science* **1998**, *280*, 1427. (b) Nolte, R. J. M.; Cornelissen, J. J. L. M.; Donners, J. J. J. M.; van Heerbeek, R.; Reek, J. N. H.; Rowan, A. E.; Sommerdijk, N. A. J. M. *Polym. Mater. Sci. Eng.* **2001**, *84*, 8. (c) Cornelissen, J. J. L. M.; Van Heerbeek, R.; Kamer, P. C. J.; Reek, J. N. H.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *Adv. Mater.* **2002**, *14*, 489. (d) Cornelissen, J. J. L. M.; Fischer, M.; van Waes, R.; van Heerbeek, R.; Kamer, P. C. J.; Reek, J. N. H.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *Polymer* **2004**, *45*, 7417. (e) de Hoog, H.-P. M.; Vriezema, D. M.; Nallani, M.; Kuiper, S.; Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M. *Soft Matter* **2008**, *4*, 1003.

(18) (a) Lim, E.; Tu, G.; Schwartz, E.; Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Huck, W. T. S. *Macromolecules* **2008**, *41*, 1945. (b) Schwartz, E.; Lim, E.; Gowda, C. M.; Liscio, A.; Fenwick, O.; Tu, G.; Palermo, V.; de Gelder, R.; Cornelissen, J. J. L. M.; Van Eck, E. R. H.; Kentgens, A. P. M.; Cacialli, F.; Nolte, R. J. M.; Samori, P.; Huck, W. T. S.; Rowan, A. E. *Chem. Mater.* **2010**, *22*, 2597.

(19) (a) Van Beijnen, A. J. M.; Nolte, R. J. M.; Drenth, W.; Hezemans, A. M. F. *Tetrahedron* **1976**, *32*, 2017. (b) van Beijnen, A. J. M.; Nolte, R. J. M.; Drenth, W.; Hezemans, A. M. F.; van de Coolwijk, P. J. F. M. *Macromolecules* **1980**, *13*, 1386. (c) Van Beijnen, A. J. M.; Nolte, R. J. M.; Naaktgeboren, A. J.; Zwikker, J. W.; Drenth, W.; Hezemans, A. M. F. *Macromolecules* **1983**, *16*, 1679. (d) Kollmar, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 8230.

(20) Cornelissen, J. J. L. M.; Donners, J. J. J. M.; de Gelder, R.; Graswinckel, W. S.; Metselaar, G. A.; Rowan, A. E.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *Science* **2001**, *293*, 676.

(21) Onouchi, H.; Okoshi, K.; Kajitani, T.; Sakurai, S.-i.; Nagai, K.; Kumaki, J.; Onitsuka, K.; Yashima, E. *J. Am. Chem. Soc.* **2007**, *130*, 229.

(22) Nolte, R. J. M.; Kuo, T.; Hall, H. K., Jr. *Synth. Met.* **1990**, *39*, 121.