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Arene-Functionalized Polyisocyanides: A Kinetic Study of Polymerization To Prepare Homopolymers and Block Copolymers

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ABSTRACT: A series of several new isocyanide monomers with substituent photosensitizers and quenchers are synthesized and characterized. The polymerization of these monomers induced by $[Ni(\eta^3\text{-allyl})(OC(O)CF_3)]_2$ (**I**) affords homopolymers and block copolymers with controllable donor and acceptor orientation and spacing. Kinetic analyses of the polymerization of the isocyanide monomers, $2\text{-}C_{10}H_7CH_2CH_2NC$ (**5**), $Me_5C_6CH_2CH_2NC$ (**6**), and $4\text{-}Me_2NC_6H_4CH_2NC$ (**10**), under N_2 result in first-order rate expressions. The propagation rate constants k_p for these monomers are calculated as 1.4×10^{-1}, 6.0×10^{-3}, and 3.6×10^{-3} $L\cdot mol^{-1}\cdot s^{-1}$, respectively, from a kinetic analysis of the preparative polymerization of a **5**–**6**–**10** triblock copolymer. Characterization of the newly synthesized homopolymers and di- and triblock copolymers (by gel permeation chromatography, infrared spectroscopy, intrinsic viscosity measurements, and NMR spectroscopy) is described.

Introduction

The synthesis and characterization of polymers for directional electron transfer and energy migration is a topic of great current interest.[1,2] Such systems are designed and studied to achieve long-lived charge separation in artificial systems, both for practical applications in material science and to mimic natural photosynthesis. In most organic polymers, however, conformational flexibility has prevented unidirectional electron transfer and/or energy migration over extended distances, because polymer folding permits the formation of energy dissipative excimers or exciplexes.[1a,3] Therefore, a rigid polymer with controllable donor and acceptor orientation and chromophore or relay spacing must be designed.[1a,4] A prototype of such a system, Figure 1, contains a series of photosensitizers and quenchers chemically attached to the rigid backbone of a block copolymer. The arrangement of the photoactive component units of each block is along an increasing or decreasing energy gradient so as to provide an anisotropic driving force for one-dimensional charge separation along the polymer chain.[5]

Polyisocyanides have been described as possessing rigid helical backbones,[6] and are hence suitable for the aforementioned studies. Although their specific conformations are sensitively dependent on the identity of the imine substituent,[6g] such polymers might be sufficiently rigid to permit intramolecular electron transfer and energy migration, either through space between the two repeated isocyanide units or through the helical backbone itself. If such a polymer were to exist as a 4/1 helix, it would exhibit a pitch of about 4 Å/turn,[6b] and the spacing between the appended groups would be fixed and well-defined.

Recent advances in nickel-mediated living polymerization of sterically unhindered isocyanides[7] have provided a possible synthetic approach to chromophore- and quencher-labeled homopolymers and block copolymers with controllable molecular weights and narrow polydispersities. Sterically unhindered polyisocyanides probably exist as random coils, but we hoped that the appended chromophores might favor the rigid helical structures that would permit spatial differentiation of the comprising blocks. In this paper, we report the synthesis and characterization of several new isocyanide monomers bearing substituent donors and acceptor groups, the preparation and characterization of homopolymers and block copolymers from these monomers, and a kinetic analysis of the living polymerizations employed in their synthesis.

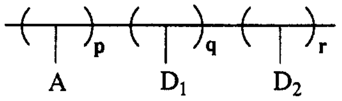

Figure 1. Polymeric array for directional electron transfer and energy migration.[5]

Results and Discussion

Synthesis of Vinyl Isocyanides and Their Polymerization. Although the syntheses of hundreds of isocyanides have been reported in the literature,[6a,8] only a few, e.g., racemic or pure enantiomers of α-methylbenzyl isocyanide, can undergo living polymerization to give polymers with controllable molecular weight and narrow polydispersity. Upon treatment with a nickel-based catalyst, i.e., $[(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)]_2$ (**I**),[4] polymers derived from isocyanides RNC in which the substituent group R is very bulky (for example, R = naphthyl or (α-naphthyl)ethyl) precipitate from the reaction solution as they are formed and are not useful in living polymerization.[9] Thus, our initial choice of a suitable series of isocyanide monomers with pendant chromophores focused on the less sterically bulky vinyl isocyanides, RCH=CHCN, with R = naphthyl or anthryl, etc.

A vinyl isocyanide bearing the $2,4,6\text{-}(CH_3)_3C_6H_2\text{-}$ substituent (**1**) has been prepared in the literature using the general procedures shown in eqs 1–4.[10] Thus, deprotonation of methyl isocyanide by treatment with *n*-butyllithium affords the lithio isocyanide, eq 1, which is condensed with an aldehyde to yield a lithium alkoxide salt, eq 2. Upon conversion to a tosylate, eq 3, elimination

$$CH_3NC + n\text{-}C_4H_9Li \rightarrow LiCH_2NC + n\text{-}C_4H_{10} \qquad (1)$$

$$LiCH_2NC + RCHO \rightarrow RCH(OLi)CH_2NC \qquad (2)$$

$$RCH(OLi)CH_2NC + TsCl \rightarrow RCH(OTs)CH_2NC + LiCl \qquad (3)$$

$$RCH(OTs)CH_2NC + KOH \rightarrow RHC{=}CHNC + KOTs + H_2O \qquad (4)$$

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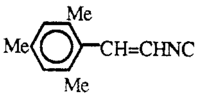
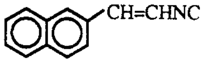
Table 1. Comparison of Absorption Data of Monomers and Homopolymers of Vinyl Isocyanides

compd	λ_{max}, nm, in CH_2Cl_2
1	232, 278
poly-1	232, 360 (br, 250–500 nm)
2	236, 260, 268, 298, 308
poly-2	232, 392 (br, 320–500 nm)
3	260, 390
poly-3	256, 396 (br, 340–600 nm)
4	212, 232, 292, 368
poly-4	246, 280, 348, 430 (br, tailed into 640 nm)

is induced by a strong base, eq 4, yielding the vinyl isocyanide. When 2-naphthaldehyde, 9-anthraldehyde, and 1-pyrenecarboxaldehyde are used in eq 2, monomers 2–4 are obtained, as described in the Experimental Section.



1



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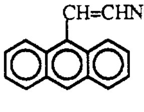

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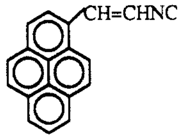

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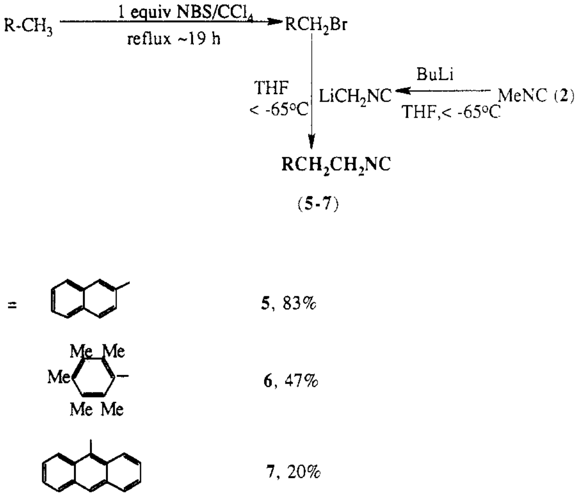
The polymerization of vinyl isocyanides is interesting because both functional groups, i.e., the isocyanide group and the double bond, are susceptible to cationic attack.[6a] In contrast, the polymerization of vinyl isocyanides by nickel(II) catalysts, though not living, takes place at the isocyanide group rather than at the carbon–carbon double bond.[11] With $NiCl_2{\cdot}6H_2O_2$ as catalyst, the polymerization of 1 affords a polymer which is insoluble in chloroform and other inert organic solvents.[11] In this study, the polymerization of 1–4 by catalyst **I** (catalyst:monomer = 1:20) in toluene is homogeneous and produces brown homopolymers that are soluble in $CHCl_3$, CH_2Cl_2, THF, or toluene, and sparingly soluble in acetone or acetonitrile. After polymerization, infrared spectra of polymers show that the $\nu_{C\equiv N}$ band at 2119–2128 cm^{-1} has disappeared, and a new band at about 1617 cm^{-1}, ascribed to $\nu_{C=N}$, is observed instead.

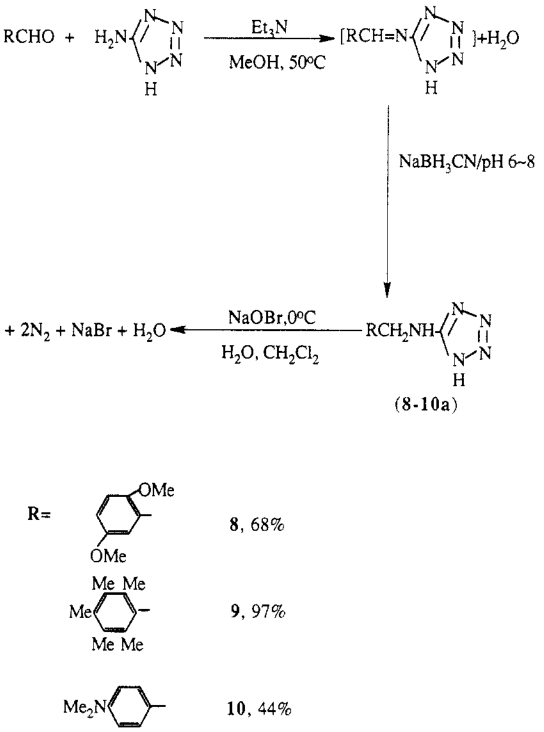
Despite their synthetic utility, however, there is a serious drawback in the use of poly(vinyl isocyanides). As shown in Table 1, the absorption spectra of the homopolymers, when compared with those of the corresponding monomers, are significantly red-shifted. Conjugation of the chromophore through the vinyl group with adjacent N=C double bonds, which is responsible for this shift, also causes polymer backbone absorption that can problematically interfere with the photophysical processes of primary interest. To avoid this effect, other saturated monomers, i.e., RCH_2CH_2NC and RCH_2NC, in which R is only modestly bulky, have been synthesized.

Synthesis of Monomers RCH_2CH_2NC and RCH_2NC. The syntheses of isocyanides RCH_2CH_2NC bearing an ethylene group between the aryl chromophore and the polymerizable isocyanide group (R = 2-naphthyl, 5; pentamethyl phenyl, 6; 9-anthryl, 7) are shown in Scheme 1. Treatment of RCH_3 with NBS yields a monobromide (5–7**a**), which is condensed with $LiCH_2NC$ to produce the corresponding isocyanides (5–7).

Scheme 1. Synthesis of Arylethyl Isocyanides



Scheme 2. Synthesis of Arylmethyl Isocyanides



Isocyanides RCH_2NC bearing a methylene group between the chromophore and isocyanide (R = 2,5-$(OMe)_2$-C_6H_3—, 8; Me_4C_6—, 9; 4-$Me_2NC_6H_4$—, 10) were prepared by the general route shown in Scheme 2, a modification of Höfle and Lange's procedure for the synthesis of benzyl isocyanide,[12] in which $NaBH_3CN$ replaced high-pressure hydrogenation as the reducing agent, permitting high selectivity under mild conditions.[13] Compounds **8a–10a** are produced with yields of 50–70%. Attempts to synthesize more bulky monomers, i.e., (9-anthryl)methyl isocyanide, failed, probably because of the difficulty in reducing the pentaazafluvene in the presence of large substituent groups.

Kinetic Analysis of the Polymerization of Isocyanides 5–10. Polymerization of (2-naphthyl)ethyl isocyanide (5) in homogeneous solution with catalyst **I** in toluene under N_2 gave the corresponding polyisocyanide in near quantitative yield (80–99%). The number average molecular weights of these polymers, determined by gel permeation chromatography against polystyrene standards, vary linearly with the initial monomer-to-catalyst ratio (Figure 2), as is characteristic of a living system. However, polymer weight distributions are rather broad, with polydispersity indexes (PDI) typically ranging from

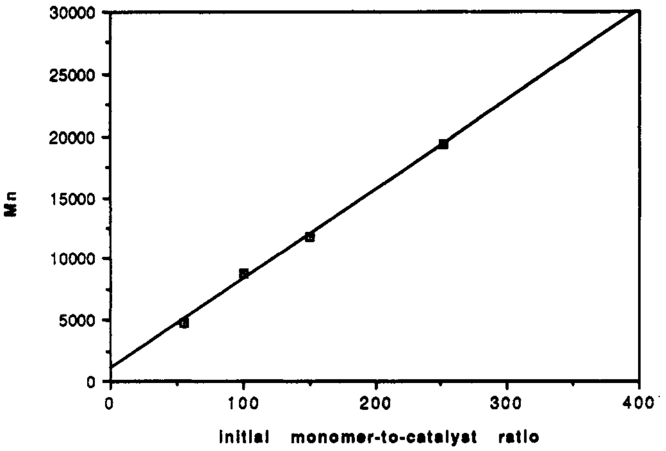


Figure 2. Dependence of the observed number average molecular weight on the initial monomer-to-catalyst ratio of homopolymers of **5**.

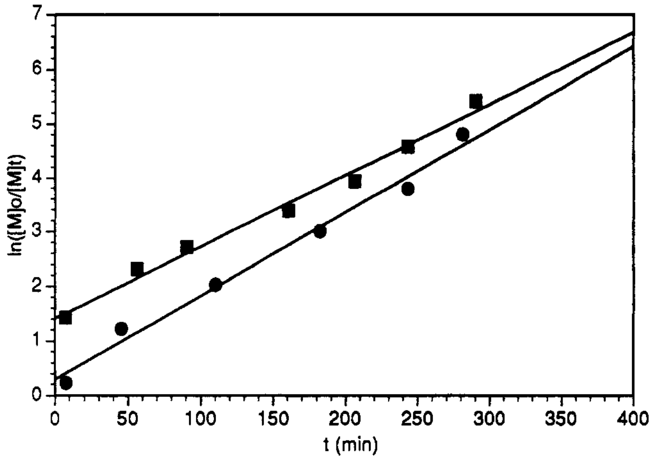


Figure 3. Dependence of the propagation rate on polymerization time for (a) polymerization of the first block of **5** ($[M]_0 = 0.5821$ M, $[I]_0 = 1.5273 \times 10^{-3}$ M, squares) and (b) polymerization of the second block of **5** [$(M]_0 = 0.3881$ M, $[I]_0 = 1.9581 \times 10^{-3}$ M, circles).

1.2 to 1.7. The necessitates a more thorough kinetic analysis of the polymerization to verify the living nature of the polymerization and to explore the possible causes of the breadth in molecular weight distribution.

The absorption spectra of homopolymers and block copolymers formed from isocyanides of RCH_2NC and RCH_2CH_2NC, when compared with those of the corresponding monomers, have no significant red-shift. This indicates that the backbone absorption observed in the poly(vinyl isocyanides), caused by conjugation of the chromophore with the N═C double bond, is eliminated here.

For a living polymerization with first-order dependence on monomer concentration,[14] a plot of the dependence of propagation rate, expressed as $\ln([M]_0/[M]_t)$, where $[M]_0$ represents the initial monomer concentration and $[M]_t$ the monomer concentration at time t, on reaction time should be linear. This behavior is indeed observed in the polymerization of monomer **5**, Figure 3 (squares). The rate constant of propagation k_p is calculated as $1.4(1) \times 10^{-1}$ $L{\cdot}mol^{-1}{\cdot}s^{-1}$. This rate constant is larger than that reported for *rac*-α-methylbenzyl isocyanide ($3.7(1) \times 10^{-2}$ $L{\cdot}mol^{-1}{\cdot}s^{-1}$), but comparable with that of the pure enantiomer of this isocyanide ($1.2(1) \times 10^{-1}$ $L{\cdot}mol^{-1}{\cdot}s^{-1}$).[7d] The linearity of the plots in Figures 2 and 3, curve a, suggest that chain transfer and chain termination are negligibly slow compared with propagation in the polymerization of **5**.[14] However, the intercept in curve a of Figure 3 is 1.4, corresponding to a 75% conversion of monomer. To determine whether this unexpected behavior was caused by contributions from the initiation rate, a kinetic analysis of a second block, where the influence of the initiation process is minimized, was carried out. After the polymerization of a first block of a 40-mer of **5**, additional monomer was added, permitting growth of a second block of 100-mer, yielding the data shown in Figure 3, curve b. (Here, *n*-mer represents the molar monomer-to-catalyst ratio in the feed solution adjusted by a factor of 2 since each equivalent of catalyst **I** produces two active chains upon addition of monomer.) The propagation rate constant for growth of the second block ($1.3(1) \times 10^{-1}$ $L{\cdot}mol^{-1}{\cdot}s^{-1}$) is nearly the same as that of the first block. However, the intercept of Figure 3b had dropped to 0.29, corresponding to only a 15% conversion of monomer. Thus, the polymerization of **5** is living and its propagation proceeds in the absence of side reactions, i.e., chain transfer and/or chain termination reaction(s), but may be competitive kinetically with the initiation rate constant.

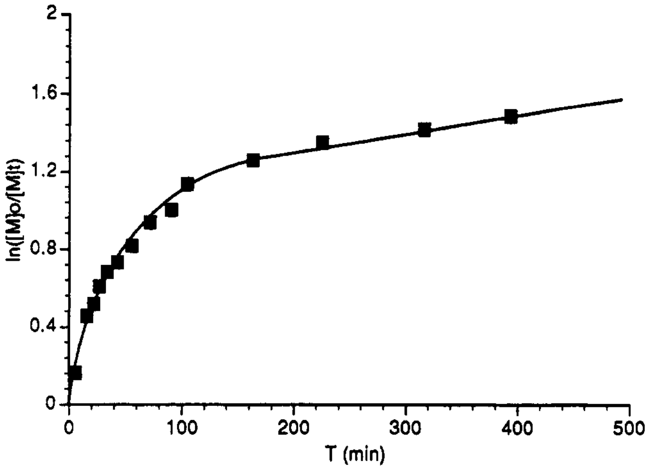


Figure 4. Dependence of propagation rate on polymerization time for polymerization of **6** ($[M]_0 = 0.1796$ M, $[I]_0 = 1.018 \times 10^{-3}$ M).

Such behavior is more clearly observed in the kinetic analysis of the homopolymer produced from **6**, Figure 4. Here, a slow initial polymerization, when compared with that of homopolymer of **5**, was followed by a linear propagation. The kinetics of the initial phase of the reaction can be described as first-order, but with a sliding rate constant that shifts from $k_i[I]_0$ to $k_p[I]_0$.[14-16] Assuming that the initiator is essentially consumed upon reaching the linear propagation phase, we should have

$$-\mathrm{d} \ln [M]/\mathrm{d}t \rightarrow k_p[I]_0$$

Thus, the propagation rate constant of the linear portion of Figure 4 can be calculated as $1.3(1) \times 10^{-2}$ $L{\cdot}mol{\cdot}s^{-1}$, i.e., 1 order of magnitude slower than that obtained for polymerization of **5** ($1.4(1) \times 10^{-1}$ $L{\cdot}mol^{-1}{\cdot}s^{-1}$).

Previously, the influence of a slow initiation on living polymerizations has been documented.[14-16] When the rate constant of initiation is lower than that of propagation, polymer chains do not start to grow simultaneously. Thus, the polymerization is accelerated as more initiation takes place, and a broad molecular weight distribution is expected.

The polymerization of **7** with catalyst **I** is heterogeneous and produces low molecular weight homopolymers that are soluble in THF and CH_2Cl_2. Currently, we are searching for other suitable solvents to carry out a homogeneous polymerization so as to obtain soluble homopolymers with higher molecular weights. The heterogeneous polymerization of **8** or **9** results in homopolymers that are insoluble in organic solvents. Infrared spectra of these homopolymers show that the $\nu_{C\equiv N}$ bands at 2145–2157 cm^{-1} have been replaced by $\nu_{C=N}$ bands at about 1610–1620 cm^{-1}. Because of the high polydispersity and the intractability resulting from their limited solubility, these polymers have not been further characterized.

The homogeneous polymerization of **10** results in homopolymers that are soluble in THF, CH_2Cl_2, $CHCl_3$, acetone, and toluene. However, no accurate data concerning molecular weight can be obtained from the GPC measurements since these polymers trail badly on a GPC column. Kinetic analysis shows that the polymerizations of **10** is first-order (with respect to monomer concentration), with an intercept of 0.48 and a propagation rate constant of $3.8(2) \times 10^{-3}$ $L{\cdot}mol^{-1}{\cdot}s^{-1}$.

On the basis of the properties of these homopolymers, three monomers were chosen to construct block copolymers because their polymerizations are living. Our kinetic analysis shows that all monomer is consumed before the second block is added. The additional chain extension, together with GPC characterization of the resulting polymers, shows that the growth of this triblock polymer occurs in three steps, with the individual blocks growing at a rate consistent only with a living polymer constructed from successive homopolymeric blocks. Monomer **5** is incorporated as the component unit of the first block (acceptor). Monomer **10** is then applied as a second block in a diblock copolymer, or as a third block in a triblock copolymer. The difference in oxidation potentials between **5** and **10** is about 790 mV, a suitable driving force for intramolecular electron transfer.[1–3] Monomer **6** is inserted as the intervening component in the triblock copolymer to probe for methods to prevent possible energy-wasting back electron transfer.[1–3,5]

The **5–6–10** block copolymer was prepared as follows. The first block of copolymer, a 100-mer of **5**, was prepared by stirring the monomer **5** with catalyst **I** for at least 12 h, with the decrease of monomer concentration being monitored by IR spectroscopy. Then a solution of the monomer precursor to the second block, a 100-mer of **6**, was added and stirred for another 36 h. All monomer of the second block having been consumed, a solution of the monomer precursor to the third block, a 100-mer of **10**, was added and the kinetic study was carried out as described above.

First-order kinetics are obtained for each successive block. The propagation rate constants are $1.4(1) \times 10^{-1}$ (intercept: 1.4), $6.0(1) \times 10^{-3}$ (intercept: 0.57), and $3.6(1) \times 10^{-3}$ $L{\cdot}mol^{-1}{\cdot}s^{-1}$ (intercept: 0.12) for the first (**5**), second (**6**), and third block (**10**), respectively. The propagation rate constant for formation of the second block, 6.0×10^{-3} $L{\cdot}mol^{-1}{\cdot}s^{-1}$, is smaller than that found in preparing the corresponding homopolymer **6**, 1.3×10^{-2} $L{\cdot}mol^{-1}{\cdot}s^{-1}$. This may be caused by the inhomogeneity of the polymerization of **6** with a precipitate being formed in the synthesis of the homopolymer and a gel-like dispersion being produced in the preparation of the block copolymer. However, the propagation rate constant of the third block of quencher **10**, $3.6(1) \times 10^{-3}$ $L{\cdot}mol^{-1}{\cdot}s^{-1}$, is the same as that observed in the preparation of the homopolymer within experiment error. GPC measurement of the isolated **5–6–10** triblock copolymer ($p = q = r = 100$) shows it to be monomodal with the number average molecular weight as 11 430 and a PDI of 1.78.

Experimental Section

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out with standard Schlenk or vacuum line techniques, or in a N_2-filled drybox. All polymerizations were carried out in toluene in the drybox in Wheaton vessels (Aldrich) that had been dried in a vacuum oven at 120 °C for 24 h prior to use.

Commercial grade solvents (benzene, toluene, tetrahydrofuran, and diethyl ether) were dried and deoxygenated by heating to reflux under N_2 at least 24 h over sodium benzophenone ketyl and were freshly distilled prior to use. Toluene and diethyl ether were further treated with three to five freeze–pump–thaw cycles before they were takend into a N_2-filled drybox and stored over potassium/sodium (4:1) alloy. Other solvents (spectrograde or HPLC grade methylene chloride, hexanes, anhydrous diethyl ether, and methanol) were used as received.

CH_3NC,[17] 2,4,6-$(CH_3)_3C_6H_2CH{=}CHNC$ (**1**),[10] and $[(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)]_2$[18] were prepared according to the published procedures. (Bromomethyl)pentamethylbenzene and (9-anthryl)methyl bromide were prepared by heating the corresponding methylarene under reflux with 1 equiv of NBS in CCl_4 for 19 h.[19] All other chemicals were purchased from Aldrich or Strem Chemicals and were used as received unless otherwise specified. Note: isocyanides must be prepared in an efficient hood because of their obnoxious odors.

Instrumentation. ^1H and proton-decoupled ^{13}C NMR spectra of all monomers were recorded in $CDCl_3$ on a QE-300 spectrometer at 300 and 75.1 MHz, respectively. ^{13}C NMR spectra of the homopolymers and diblock polymers were recorded overnight in $CDCl_3$ on an NT-360 MHz spectrometer operating at 90.1 MHz. Infrared spectra were obtained on a Nicolet 510P FT-IR spectrometer. Absorption spectras were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Gel permeation chromatography (GPC) characterization polymers was carried out, using a THF eluent, on a Waters 590 HPLC. Separations were effected by 10^4, 10^3, and 500 Å Waters Ultrastyragel columns, and molecular weights were calibrated relative to polystyrene standards. Melting points (uncorrected) were determined using a Melt-temp apparatus. High-resolution mass spectra of isocyanide monomers were recorded on a VG ZAB2-E (VG Analytical LTD., Manchester, U.K.) mass spectrometer.

General Procedure for the Preparation of Vinyl Isocyanides 2–4. A solution of 2.65 mL (2.00 g, 45 mmol) of MeNC in 100 mL of THF was placed into a 500 mL three-neck flask equipped with a low-temperature thermometer, a magnetic stirrin bar, a 50 mL pressure-equalizing dropping funnel, and a N_2 inlet. After having been cooled in a dry ice bath, 28.5 mL (45 mmol) of 1.6 N butyllithium in hexanes was added at a rate such that the temperature of the reaction mixture did not exceed −65 °C. The resulting cold solution having been stirred for an additional 5 min, (isocyanomethyl)lithium was treated with a solution of 42 mmol of araldehyde in 40 mL of THF at a rate such that the temperature remained below −65 °C. After stirring for an additional 15 min, a solution of 8.20 g (43 mmol) of *p*-toluenesulfonyl chloride in 30 mL of THF was added dropwise. The reaction mixture was stirred at a temperature below −65 °C for an additional 15 min after the addition of *p*-toluenesulfonyl chloride was complete. The dry ice bath was then removed, and the reaction mixture was allowed to warm to 22 °C before being kept at 30–35 °C with a temperature-controlled water bath. At this temperature, a solution of 4.35 g (66.0 mmol) of 85% potassium hydroxide in 30 mL of methanol was added over a period of 20 min. After the solution was stirred for an additional 45 min, the solvents (THF, hexanes, and methanol) were removed under a water aspirator vacuum. Distilled H_2O (100 mL) was then added, and the suspended yellow solid was extracted with diethyl ether (4×). The combined extracts were dried over anhydrous $MgSO_4$ at −20 °C. Upon removal of solvent, the resulting brown-yellow solid was washed with 25 mL of hexanes (4×) before being vacuum-dried overnight.

Preparation of (2-Naphthyl)vinyl Isocyanide (2). From 6.69 g (42 mmol) of 2-naphthaldehyde was obtained 3.0 g (40%) of an off-white solid. Mp: 120–121 °C. ^1H NMR ($CDCl_3$): δ 7.82 (4 H, m), 7.52 (3 H, m), 7.08 (1 H, d, $J = 14.4$ Hz), 6.37 (1 H, d, $J = 14.4$ Hz). ^{13}C ($CDCl_3$): δ 165.51 (t, $J_{N\equiv C} = 5.0$ Hz), 136.66 (s), 133.81 (s), 133.28 (s), 130.24 (s), 128.85 (s), 128.27 (s), 128.05 (s), 127.76 (s), 127.11 (s), 126.88 (s), 122.32 (s), 110.85 (t, $J_{\equiv C-N}$ = 11.3 Hz). IR (Nujol, NaCl): $\nu_{N\equiv C}$ 2125 cm^{-1}. Absorption spectrum (CH_2Cl_2; λ_{max}, nm; ϵ_{max}, M^{-1} cm^{-1}): 236 (18 590), 260- (44 750), 268 (48 580), 298 (28 110), 308 (29 980). High resolution mass: calcd for $C_{13}H_{10}N$, 180.0813; found, 180.0814.

Preparation of (9-Anthryl)vinyl Isocyanide (3). From 8.66 g (42 mmol) of 9-anthraldehyde was obtained 2.20 g (23%) of yellow needle crystals. Mp: 165.5–166.0 °C. ^1H NMR ($CDCl_3$): δ 8.45 (1 H, s), 8.14 (2 H, d, J = 8.1 Hz), 8.01 (2 H, d, J = 8.1 Hz), 7.80 (1 H, d, J = 14.4 Hz), 7.52 (4 H, m), 6.18 (1 H, d, J = 14.4 Hz). ^{13}C ($CDCl_3$): δ 165.48 (s), 133.23 (s), 130.99 (s), 129.34 (s), 128.77 (s), 128.34 (s), 126.46 (s), 125.94 (s), 125.30 (s), 124.59 (s), 117.42 (t, $J_{\equiv C-N}$ = 10.4 Hz). IR (Nujol, NaCl): ν_{NC} 2128 cm^{-1}. Absorption spectrum (CH_2Cl_2; λ_{max}, nm; ϵ_{max}, M^{-1} cm^{-1}): 260 (135 900), 390 (5900). High resolution mass: calcd for $C_{17}H_{12}N$, 230.0970; found, 230.0968.

Preparation of (1-Pyrenyl)vinyl Isocyanide (4). From 9.67 g (42 mmol) of 1-pyrenecarboxaldehyde was obtained 3.47 g (33%) of a yellow solid. Mp: 132.5–133.5 °C. ^1H NMR ($CDCl_3$): δ 8.13 (10 H, m), 6.48 (1 H, d, J = 14.1 Hz). ^{13}C ($CDCl_3$): δ 165.21 (s), 133.70 (s), 132.02 (s), 131.04 (s), 130.42 (s), 128.36 (s), 128.29 (s), 128.17 (s), 127.01 (s), 126.17 (s), 125.90 (s), 125.82 (s), 125.58 (s), 124.65 (s), 124.42 (s), 124.17 (s), 122.80 (s), 121.70 (s), 111.95 (t, $J_{\equiv C-N}$ = 10.7 Hz). IR (Nujol, NaCl): $\nu_{N\equiv C}$ 2119 cm^{-1}. Absorption spectrum (CH_2Cl_2; λ_{max}, nm; ϵ_{max}, M^{-1} cm^{-1}): 212 (9090), 232 (54 430), 292 (38 440), 368 (47 210). High resolution mass: calcd for $C_{19}H_{12}N$, 254.0970; found, 254.0960.

General Procedure for the Preparation of Arylethyl Isocyanide (Scheme 1). To a cold solution of (isocyanomethyl)-lithium (32 mmol), prepared as above, was added 32.0 mmol of (bromomethyl)arene in 30 mL of THF at such a rate that the temperature remained below –65 °C. The solution having been stirred for 1 h, the dry ice bath was removed and the reaction mixture was allowed to warm to 22 °C. All volatile materials were removed under vacuum (50 μm) to give an orange-red liquid residue. Distilled H_2O (100 mL) was added, and the resulting aqueous solution was extracted with diethyl ether (4×). The combined extracts were washed with aqueous NaCl and were dried over anhydrous $MgSO_4$ at –20 °C. Upon removal of solvent under a water aspirator vacuum, the solid was recrystallized from hot hexanes.

Preparation of (2-Naphthyl)ethyl Isocyanide (5). From 7.10 g (32 mmol) of 2-bromonaphthalene was obtained 4.81 g of a white solid (83%). Mp: 69.5–70.0 °C. IR (KBr): 3057 (w), 2923 (w), 2155 (s), 1599 (w), 1508 (w), 1451 (w), 1370 (w), 1275 (w), 993 (w), 968 (w), 954 (w), 900 (m), 864 (m), 829 (s), 808 (s) cm^{-1}. ^1H ($CDCl_3$): δ 7.82 (m, 3 H), 7.68 (s, 1 H), 7.49 (m, 2 H), 7.31 (d, 1 H), 3.67 (t, 2 H, J = 6.6 Hz), 3.12 (t, 2 H, J = 6.6 Hz). ^{13}C ($CDCl_3$): δ 156.60 (t, $J_{N\equiv C}$ = 3.9 Hz), 133.97 (s), 133.35 (s), 132.41 (s), 128.44 (s), 127.59 (s), 127.53 (s), 127.33 (s), 126.54 (s), 126.24 (s), 125.81 (s), 42.77 (t, J_{-CH_2-N} = 5.6 Hz), 35.69 (s). Absorption spectrum (THF; λ_{max}, nm; ϵ_{max}, M^{-1}, cm^{-1}): 226 (106 010), 268 (12 640), 280 (10 660), 292 (6080). High resolution mass: calcd for $C_{13}H_{11}N$, 181.0891; found, 181.0893.

Preparation of (Isocyanoethyl)pentamethylbenzene (6). From 5.30 g (22.4 mmol) of (bromomethyl)pentamethylbenzene was obtained 2.12 g (47%) of an off-white solid. Mp: 57.0–58.0 °C. IR (KBr): 3441 (w), 2989 (m), 2948 (w), 2366 (w), 2154 (s), 1432 (m), 1374 (w), 1348 (w), 1245 (w), 1063 (w), 1054 (m), 990 (m), 967 (w), 942 (w), 921 (w), 906 (w), 888 (w), 868 (w), 829 (m), 812 (w) cm^{-1}. ^1H ($CDCl_3$): δ 3.41 (t, 2 H, J = 8.1 Hz), 3.18 (t, 2 H, J = 8.1 Hz), 2.25 (s, 6 H), 2.22 (s, 6 H), 2.20 (s, 3 H). ^{13}C ($CDCl_3$): δ 156.12 (s), 134.13(s), 132.99 (s), 132.02 (s), 130.15 (s), 40.64 (t, J_{-CH_2-N} = 17.7 Hz), 30.81 (s), 16.92 (s), 16.83 (s), 16.53 (s). Absorption spectrum (THF; λ_{max}, nm; ϵ_{max}, M^{-1} cm^{-1}): 236 (2790), 278 (1360). High resolution mass: calcd for $C_{14}H_{19}N$, 201.1518; found, 201.1514.

Preparation of (9-Anthryl)ethyl Isocyanide (7). From 3.640 g (13.4 mmol) of 9-(bromomethyl)anthracene was obtained 0.62 g (20%) of a yellow product. Mp: 107.5–108.5 °C. IR (KBr): 3437 (m), 3052 (m), 2953 (m), 2147 (s), 1667 (w), 1624 (m), 1524 (w), 1485 (w), 1445 (s), 1347 (w), 1181 (w), 1158 (m), 1104 (w), 1019 (w), 956 (w), 886 (s), 841 (m) cm^{-1}. ^1H ($CDCl_3$): δ 8.42 (s, 1 H), 8.20 (d, 2 H, J = 8.7 Hz), 8.02 (d, 2 H, J = 8.7 Hz), 7.57 (t, 2 H, J = 6.6 Hz), 7.48 (t, 2 H, J = 6.6 Hz), 4.09 (t, 2 H, J = 7.8 Hz), 3.75 (t, 2 H, J = 7.8 Hz). ^{13}C ($CDCl_3$): δ 157.19 (s), 131.43 (s), 129.82 (s), 129.47 (s), 127.73 (s), 127.50 (s), 126.55 (s), 125.07 (s), 123.19 (s), 41.45 (t, J_{-CH_2-N} = 20.7 Hz), 27.96 (s). Absorption spectrum (THF; λ_{max}, nm; ϵ_{max}, M^{-1} cm^{-1}): 262 (14 770), 352 (4350), 370 (6600), 390 (6160). High resolution mass: calcd for $C_{17}H_{13}N$, 231.1048; found, 231.1039.

General Procedure for the Preparation of Arylmethyl Isocyanides (Scheme 2). Into a 500 mL three-neck flask were placed 8.60 g (0.1 mol) of 5-aminotetrazole (dehydrated by heating over P_2O_5 at 100 °C under reduced pressure (50 μm for 4 h before use) and 13.9 mL (0.1 mol) of triethylamine in 50 mL of absolute methanol. Having been stirred at 50 °C for 15 min, the resulting solution (pH 8) was cooled before 4.40 g (0.070 mole) of $NaBH_3CN$ in 20 mL of absolute methanol was added. The resulting mixture was stirred for 19–24 h. All volatile materials were then evaporated at 60 °C under a water aspiratory, yielding a yellow gummy residue which was triturated with 100 mL of hot water. Aqueous 3 N HCl was then added dropwise until pH 3 was reached. The resulting precipitate was filtered and washed with 500 mL (3×) of distilled water and 75 mL (2×) of absolute EtOH, before being vacuum-dried overnight. Yield: **8a**, 50%. IR (KBr): 3269 (m), 3062 (w), 2955 (w), 2934 (w), 2880 (w), 2835 (w), 1644 (s), 1538 (w), 1506 (s), 1465 (m), 1441 (m), 1422 (m), 1232 (s), 1217 (s), 1186 (m), 1088 (w), 1064 (m), 1048 (s), 808 (w), 803 (m) cm^{-1}. **9a**: 70%. IR (KBr): 3242 (m), 2916 (s), 2854 (s), 1690 (s), 1568 (m), 1420 (m), 1380 (m), 1287 (s), 1255 (m), 1074 (m), 1002 (m), 846 (m) cm^{-1}. **10a**: 54%. IR (KBr): 3257 (m), 1611 (s), 1528 (s), 1467 (w), 1445 (w), 1358 (m), 1254 (w), 1237 (w), 1192 (m), 1168 (m), 1126 (w), 1048 (m), 992 (w), 949 (w), 808 (m) cm^{-1}.

Into a 500 mL flask equipped with a magnetic stirrer and a pressure-equalizing funnel were placed 5.0 g of the above synthesized 5-aminotetrazole derivative, 45 mL of 10% aqueous NaOH, and 50 mL of CH_2Cl_2. The mixture was cooled to 0 °C, and a solution of 1 equiv of aqueous NaOBr[20] was added, with vigorous stirring, over a period of 10–15 min. After being stirred for 30–60 min, the organic layer was separated and the aqueous phase extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with aqueous NaCl (2 × 50 mL) and dried over anhydrous $MgSO_4$ at –20 °C. The drying agent was removed by filtration, and the solvent was vacuum-evaporated to give a yellow residue that was recrystallized from hot hexanes.

Preparation of 2,5-Dimethoxybenzyl Isocyanide (8). From 5.0 g (21.3 mmol) of **8a** was obtained 2.56 g (68%) of pale-yellow needle crystals. Mp: 54.5–55.5 °C. IR (KBr): 2842 (w), 2157 (m), 1500 (s), 1464 (w), 1450 (m), 1446 (m), 1436 (m), 1309 (w), 1288 (s), 1248 (m), 1221 (s), 1196 (m), 1187 (m), 1163 (w), 1120 (m), 1052 (m), 1022 (m), 955 (m), 858 (m), 816 (m) cm^{-1}. ^1H ($CDCl_3$): δ 7.44 (d, 1 H, J = 2.4 Hz), 7.26 (d, 1 H, J = 2.4 Hz), 7.21 (s, 1 H), 50.4 (s, 2 H), 4.22 (s, 6 H). ^{13}C ($CDCl_3$): δ 157.20 (t, $J_{N\equiv C}$ = 9.2 Hz), 153.62 (s), 150.17 (s), 121.58 (s), 113.77 (s), 113.71 (s), 111.13 (s), 55.71 (s), 41.02 (t, J_{-CH_2-N} = 6.8 Hz). Absorption spectrum (THF; λ_{max}, nm; ϵ_{max}, M^{-1} cm^{-1}): 236 (2910), 296 (3660). High resolution mass: calcd for $C_{10}H_{11}NO_2$, 177.0790; found, 177.0795.

Preparation of (Isocyanomethyl)pentamethylbenzene (9). From 5.0 g (20.4 mmol) of **9a** was obtained 3.70 g (97%) of a pale-yellow solid. Mp: 65.5–67.0 °C. IR (KBr): 2920 (m), 2145 (s), 1690 (m), 1447 (m), 1336 (w), 1287 (w), 1069 (w), 904 (m), 811 (w) cm^{-1}. ^1H ($CDCl_3$): δ 4.61 (s, 2 H), 2.40 (s, 3 H), 2.33 (s, 6 H), 2.23 (s, 6 H). ^{13}C ($CDCl_3$): δ 155.42 (s), 135.97 (s), 133.13 (s), 132.35 (s), 127.28 (s), 41.09 (t, J_{-CH_2-N} = 7.1 Hz), 17.06 (s), 16.70 (s), 16.28 (s). Absorption spectrum (THF; λ_{max}, nm; ϵ_{max}, M^{-1} cm^{-1}): 236 (2050), 270 (2680), 310 (470). High resolution mass: calcd for $C_{13}H_{17}N$, 187.1361; ound, 187.1368.

Preparation of 4-(Isocyanomethyl)-*N,N'*-dimethylaniline (10). From 5.0 g (24.6 mmol) of **9a** was obtained 1.74 g (44%) of an off-white solid. Mp: 47.5: 47.5–48.0 °C. IR (KBr): 2892 (m), 2814 (m), 2148 (s), 1665 (w), 1618 (m), 1600 (m), 1568 (w), 1531 (s), 1483 (w), 1442 (m), 1364 (m), 1232 (m), 1188 (m), 1168 (m), 1066 (w), 912 (w), 823 (w), 802 (s) cm^{-1}. ^1H ($CDCl_3$): δ 7.62 (d, 2 H, J = 8.7 Hz), 6.78 (d, 2 H, J = 8.7), 4.57 (s, 2 H), 3.02 (s, 6 H). ^{13}C ($CDCl_3$): δ 150.53 (s), 127.91 (s), 119.93 (s), 112.49 (s), 110.97 (s), 45.17 (t, J_{-CH_2-N} = 7.1 Hz), 40.45 (s). Absorption spectrum (THF; λ_{max}, nm; ϵ_{max}, M^{-1} cm^{-1}): 214 (28 320), 264

(40 280), 306 (5100). High resolution mass: calcd for $C_{10}H_{12}N$, 160.1000; found, 160.0997.

General Procedure for the Polymerization of Vinyl Isocyanides 1–4. In a drybox 10 mg (0.23 mmol) of catalyst **I** was dissolved in 1.5 mL of toluene in a 10 mL Wheaton bottle, producing an orange solution. A solution of 87 mg (0.46 mmol) of **2** in 2 mL of toluene was added dropwise to the vigorously stirred catalyst solution. The resulting dark brown-red solution was stirred for 3 h. The polymerization was then quenched with 0.50 mL of 2 M KOH/MeOH, and the resulting solution was stirred for an additional 30 min. The resulting brown-red solution was added dropwise to 100 mL of methanol containing 0.5 g of KOH. The precipitated brown-red polymer was isolated by filtration, washed with 10 mL of methanol, and vacuum-dried for 3 h to yield 81 mg (93%) of brown powder. IR (Nujol, NaCl, cm^{-1}): 2850 (s), 1617 (m), 1465 (s), 1377 (s), 946 (w), 855 (w), 814 (w). GPC (THF, against polystyrene standards): M_n = 2730, PDI = 1.62.

Polymerization of 5. In a drybox 2.5 mg (0.005 874 mmol) of catalyst **I** was dissolved in 0.5 mL toluene in a 10 mL Wheaton bottle to give an orange solution. A solution of **5** (127 mg for a 55-mer, 213 mg for a 100-mer, 319 mg for a 150-mer, and 537 mg for a 252-mer) in 1.5–3.5 mL of toluene was added dropwise to the vigorously stirred catalyst solution. The resulting brown-red solution was stirred for 24–36 h and then quenched by adding dropwise to vigorously stirred 0.02 M KOH/MeOH at −60 °C. The precipitated brown polymer was isolated by filtration, washed with 10 mL of methanol, and reprecipitated twice from THF/methanol at −70 °C to give a light-brown powder. Yield: 80–99%. IR (KBr): 3050 (m), 2919 (m), 1633 (m), 1601 (m), 1509 (m), 1440 (w), 1355 (w), 1125 (w), 1018 (w), 891 (w), 854 (w), 815 (s) cm^{-1}. ^1H ($CDCl_3$, 100-mer): δ 7.20 (br), 3.44 (br), 2.39 (br). ^{13}C ($CDCl_3$, 100-mer): δ 165 (br, weak), 137.3 (br), 133.2, 131.9, 127.5, 127.3, 126.5, 125.5, 125.0, 56.2 (br), 37.3 (br). Absorption spectrum (THF; λ_{max}, nm; 100-mer): 232, 276 (br, tailed into ~300 nm). GPC (THF, against polystyrene standards: M_n = 4740 (55-mer), 8720 (100-mer), 11 780 (150-mer), 19 360 (252-mer); PDI = 1.48 (55-mer), 1.65 (100-mer), 1.44 (150-mer), 1.50 (252-mer). Intrinsic viscosity (toluene, 25.1 ± 0.1 °C): 11.9 (55-mer), 19.1 mL/g (150-mer).

Polymerization of 6. In a drybox 1.5 mg (0.003 524 mmol) of catalyst **I** was dissolved in 1.0 mL of toluene in a 5 mL Wheaton bottle. A solution of **6** (50.0 mg, 0.2483 mmol) in 1.5 mL of toluene was added dropwise to the vigorously stirred catalyst solution. The resulting brown solution contained a small amount of yellow precipitate. This mixture was stirred for 24 h and then was quenched by adding dropwise to a vigorously stirred 0.02 M solution of KOH/MeOH at −60 °C. The precipitated brown polymer was isolated by filtration, washed with methanol, and vacuum dried. Yield: 55%, IR (KBr): 2910 (s), 1634 (m), 1449 (s), 1382 (m), 1360 (m), 1061 (s), 994 (m) cm^{-1}. Absorption spectrum (THF; λ_{max}, nm): 238, 274 (br, tailed into ~ 200 nm). GPC (THF, against polystyrene standards): M_n = 3380, PDI = 1.27.

Polymerization of 7. In a drybox 3.5 mg (0.008 224 mmol) of catalyst **I** was dissolved in 0.5 mL of toluene in a 5 mL Wheaton bottle. A solution of **7** (124 mg, 0.5361 mmol) in 1.5 mL of toluene was added dropwise to the vigorously stirred catalyst solution. A yellow precipitate formed during the addition of monomer solution. This mixture was stirred for 24 h and then was quenched by adding dropwise to vigorously stirred 0.02 M KOH/MeOH at −60 °C. The precipitated brown polymer was isolated by filtration, washed with methanol, and vacuum-dried. Yield: 51%. IR (KBr): 3049 (s), 1623 (s), 1523 (m), 1444 (s), 1346 (m), 1158 (m), 802 (s), 882 (s), 838 (s) cm^{-1}. Absorption spectrum (THF; λ_{max}, nm): 266, 356, 374, 304. GPC (THF, against polystyrene standards): M_n = 1135, PDI = 1.60.

Polymerization of 8 and 9. In a drybox 5.0 mg (0.011 75 mmol) of catalyst **I** was dissolved in 1.0 mL of toluene in a 5 mL Wheaton bottle. A solution of monomer **8** (174 mg, 0.982 mmol) of monomer **9** (176 mg, 0.940 mmol) in 2.0 mL of toluene was added dropwise to the vigorously stirred catalyst solution. Yellow precipitate formed during the addition of monomer solution. This mixture was stirred for 20–24 h and then quenched by adding dropwise to vigorously stirred 0.02 M KOH/MeOH. The precipitated brown polymer was isolated by filtration, washed with methanol, and vacuum-dried. Yield: 50–60%. Both polymers cannot dissolve in nonreactive organic solvents. IR (KBr, cm^{-1}): (poly-**8**) 2996 (m), 2943 (m), 2832 (m), 1678 (m), 1637 (m), 1611 (m), 1502 (s), 1466 (s), 1430 (s), 1297 (m), 1278 (m), 1231 (s), 1219 (s), 1180 (m), 1158 (m), 1121 (w), 1047 (s), 943 (w), 857 (m), 831 (w); (poly-**9**) 2996 (m), 2920 (m), 1680 (m), 1618 (m), 1450 (s), 1385 (s), 1212 (w), 1134 (w), 1062 (w), 1008 (w), 883 (w), 858 (w), 822 (w).

Polymerization of 10. In a drybox 2.5 mg (0.005 874 mmol) of catalyst **I** was dissolved in 1.0 mL of toluene in a 5 mL Wheaton bottle. A solution of **10** (188 mg, 1.175 mmol) in 1.0 mL of toluene was added dropwise to the vigorously stirred catalyst solution. The resulting brown solution was stirred for 36 h and then quenched by adding dropwise to vigorously stirred 0.02 M KOH/MeOH at −60 °C. The precipitated brown polymer was isolated by filtration, washed with methanol, and reprecipitated from THF/methanol at −70 °C. Yield: 65%. IR (KBr): 2976 (m), 2935 (m), 2886 (m), 2856 (m), 2822 (m), 2782 (m), 1614 (s), 1581 (s), 1500 (s), 1452 (m), 1346 (m), 1307 (m), 1226 (w), 1190 (m), 1164 (m), 1094 (m), 1094 (m), 1049 (w), 948 (m), 816 (m) cm^{-1}. Absorption spectrum (THF; λ_{max}, nm): 232, 262, 310 (sh, tailed into 340 nm). GPC (THF, against polystyrene standards): peak trailing badly, no accurate measurement was obtained.

Preparation of Copolymer $(2\text{-}C_{10}H_7CH_2CH_2NC)_m(4\text{-}Me_2NC_6H_4CH_2NC)_n$ (5–10 Diblock). The following represents a typical procedure. In a N_2-filled drybox 1.3 mg (0.003 055 mmol) of catalyst **I** was dissolved in 0.5 mL of toluene in a 5 mL Wheaton bottle. A solution of 177.2 mg (0.9777 mmol) of **5** in 1.5 mL of toluene was added dropwise to the vigorously stirred catalyst solution. The resulting brown-red solution was stirred for 24 h before a solution of 39.2 mg (0.2447 mmol) of **10** in 1.0 mL of toluene was added dropwise. The brown solution mixture was stirred at room temperature for an additional 48 h. It was quenched by adding dropwise to vigorously stirred 0.02 M KOH/MeOH at −40 °C. The precipitated gray polymer was isolated via filtration, washed with 10 mL of methanol, and reprecipitated from THF/methanol at −70 °C to give a light gray powder. Yield: 60%. IR (KBr): 3050 (m), 2927 (m), 2855 (m), 2823 (m), 2776 (m), 1633 (m), 1614 (m), 1601 (s), 1524 (s), 1505 (s), 1443 (m), 1347 (s), 1269 (w), 1164 (m), 1093 (w), 1047 (w), 1018 (w), 947 (w), 854 (m), 814 (s) cm^{-1}. Absorption spectrum (THF; λ_{max}, nm): 224, 260 (sh, tailed into 300 nm). ^{13}C ($CDCl_3$): δ 165 (br, weak), 150 (br, weak), 137.2 (br), 133.3 (br), 131.8 (br), 129.7, 127.5, 127.3, 126.4, 125.5, 125.0, 119.2 (br), 112.8, 56.2 (br), 45.3, 40.9, 37.5 (br). GPC (THF, against polystyrene standards): m = 160, n = 40, M_n = 5200, PDI = 1.30; m = n = 55, M_n = 3670, PDI = 1.76; m = n = 40, M_n = 1720, PDI = 1.38; m = 20, n = 40, M_n = 1110, PDI = 1.33.

Preparation of Copolymer $(2\text{-}C_{10}H_7CH_2CH_2NC)_{100}(Me_5C_6CH_2NC)_{100}(Me_2NC_6H_4CH_2NC)_{100}$ (5–6–10 Triblock). In a N_2-filled drybox 2.5 mg (0.005 874 mmol) of catalyst **I** was dissolved in 0.5 mL of toluene in a 10 mL Wheaton bottle. A solution of 213 mg (1.175 mmol) of **5** was added dropwise to the vigorously stirred catalyst solution. The resulting brown-red solution was stirred for 12 h. The solution of the second block of **6** (237 mg, 1.175 mmol) was added dropwise and stirred for 36 h to give a thick gel-like brown solution. Then a solution of the third block of **10** (188 mg, 1.175 mmol) in 2.0 mL of toluene was added dropwise. The brown solution mixture thus obtained was stirred for an additional 48 h. The resulting brown solution was quenched by adding dropwise to vigorously stirred 0.02 M KOH/MeOH at −40 °C. The precipitated brown polymer was isolated via filtration, washed with 10 mL (×2) of methanol, and reprecipitated from THF/methanol at −70 °C to give a brown powder. Yield: 60%. IR (KBr): 3056 (m), 3020 (w), 2914 (s), 2855 (m), 1633 (m), 1600 (s), 1523 (m), 1505 (s), 1442 (m), 1351 (m), 1271 (w), 1166 (w), 1153 (w), 1124 (w), 1092 (w), 1054 (m), 1019 (m), 946 (m), 887 (m), 856 (m), 815 (s) cm^{-1}. Absorption spectrum (THF; λ_{max}, nm): 226, 262 (br, tailed into 300 nm). GPC (THF, against polystyrene standards): M_n = 11430, PDI = 1.78.

Kinetic Measurements. Kinetic data were obtained by periodically removing aliquots from polymerization reactions carried out at 22 ± 1 °C in a N_2-filled drybox, diluting them with toluene to a known volume (90–100 μL), and recording the absorbance intensity of the isocyanide stretch of unreacted monomer by IR spectroscopy. Isocyanide concentrations were determined with the use of an empirical calibration curve (absorbance vs concentration) of suitable monomers in toluene. Kinetic analysis of the polymerization of **6** was carried out under an Ar atmosphere on the Schlenk line instead of in the drybox.

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