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Mechanistic Studies on the Nickel-Catalyzed Polymerization of Isocyanides

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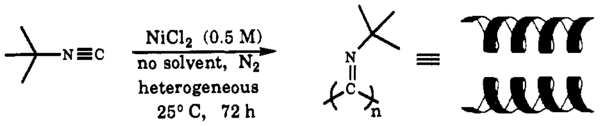
Abstract: All mechanistic aspects of nickel-mediated isocyanide polymerizations have been examined experimentally. Chain initiation has been studied by $^{13}C\{^1H\}$ NMR at low temperature using a living polymerization system. Chain propagation has been examined by cyclic voltammetry, ESR spectroscopy, magnetic susceptibility measurements, temperature dependent kinetic studies, and substituent effect analysis. The chain-propagation studies were performed on both living and classical heterogeneous systems and were found to be invariant with respect to the type of nickel initiator used. Finally, chain-transfer reactions were studied by NMR, kinetic studies, substituent effect analyses, and chemical studies. Comprehensive mechanistic schemes have been derived from the experimental data and are presented as the most probable reaction pathways.

Introduction

Polyisocyanides were first synthesized over 20 years ago by Millich and co-workers in Missouri.[1] Using carefully prepared acid-treated ground glass, he was able to produce high molecular weight polymers which proved to possess many interesting properties. Perhaps the most striking of which was restricted rotation in the polymer backbone which caused polymers with bulky substituents (e.g. poly(*tert*-butyl isocyanide)) to adopt extended helical chain conformations that were stable in solution.[2] The inherent chirality in these helical polymers provided the main driving force for further studies on these materials. Unfortunately, these polymerizations were heterogeneous and only "modestly" reproducible, making mechanistic studies and the controlled synthesis of well-defined polymers very difficult.[1a]

A significant advancement in the synthesis of polyisocyanides was made by Drenth and co-workers in the early 1970's by the implementation of transition-metal catalysts for the reaction. Simple salts of nickel(II) were found to be catalysts for the heterogeneous polymerization of sterically unhindered isocyanides (eq 1).[3] Subsequently, nearly all attempts to prepare polyisocyanides for studies on their helical behavior, nonlinear optical behavior, ion channel properties, and diastereomeric selectivity to favor growth of single-handed helices have employed the nickel-catalyzed reaction.[4] The proposed polymerization mechanism involved successive insertions of coordinated isocyanide monomers into the propagating iminoacyl group attached to a square planar nickel(II) (Scheme I).[3b,3c,5] This proposed mechanism was later used to explain and/or verify results for some finer aspects of polymerization such as stereoselection in chiral polymerizations and helix-sense selectivity in polymerizations of bulky monomers.[6]



(1)

When we began to study isocyanide polymerizations a few years ago, we very quickly noticed many discrepancies between our results and this proposed mechanism (*vide infra*). In particular, we observed the presence of nickel(I) under polymerization conditions as well as a strong dependence of the reaction on O_2.[7] These results led to the development of a homogeneous living polymerization system based on $[(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)]_2$ (**I**) which can be utilized to prepare polyisocyanides in a very controlled fashion.[8] The lack of side reactions in this polymerization system has allowed us to study the details of the pure chain propagation mechanism both with and without the presence of O_2. By varying the structure of the isocyanide monomer, we were also able to examine chain-transfer reactions in the polymerization process. We now report the results of these studies and their implications on polyisocyanide synthesis.

Initial Results and Observations

Literature reports describe the quantitative polymerization of unhindered isocyanides by nickel(II) salts in ethanol in a few (~5) hours.[4] Our attempts to reproduce these results under N_2

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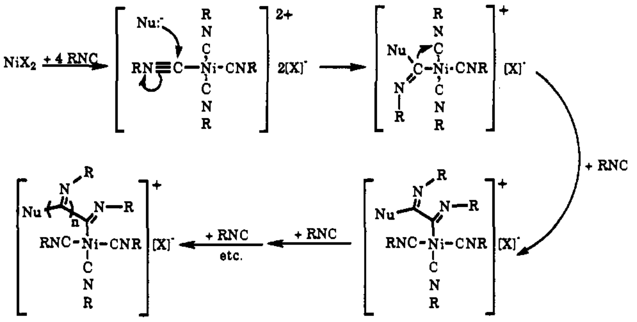
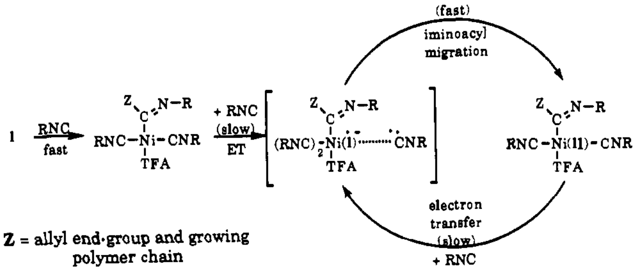
Scheme I. Proposed Polymerization Mechanism



Scheme II. Polymerization under Nitrogen.



in either THF, ethanol, or water under scrupulously anaerobic conditions gave only low yields of polymer (~50–60%) after relatively long reaction periods (~20 h).[7] Subsequent investigations led to the discovery that polymerizations run under 1 atm of air actually give high yields (>90%) of polymer in less than 1 h. Passing O_2 over a sluggish polymerization run under N_2 led to an immediate increase in polymer formation.

Somewhat similar results were observed by Millich and coworkers in their acid-catalyzed isocyanide polymerization systems.[1] They had observed that O_2, as well as free radical sources (i.e. peroxides), cocatalyzed their polymerizations, leading to higher yields of polymer.[9] Although the mechanism of the acid-catalyzed systems is unknown, the polymerizations most probably proceed through cationic intermediates (BF_3 etherate is also known to polymerize isocyanides).[10] The often low yields of polymer and irreproducibility in these systems have made in-depth investigations very difficult. Since free radicals alone have proven unable to polymerize isocyanides,[11] the role of O_2 and other radicals in these presumably cationic systems becomes even more mysterious. We hope to illustrate that the role of O_2 in nickel-catalyzed isocyanide polymerizations can be defined precisely and delegated to a small number of potential processes.

The addition of O_2 to polymerization reactions, however, at best represents a compromise. When O_2 was bubbled continuously through a polymerization mixture, the polymer yield decreased dramatically. Similarly, a solution of *tert*-butyl isocyanide and *trans*-$NiCl_2[CNC(CH_3)_3]_2$ in THF gave, after purging with O_2 for 1 h, nearly quantitative oxidation to the corresponding *tert*-butyl isocyanate. To account for the behavior of O_2, we initially believed that O_2 might be oxidizing nickel(II) to a nickel(III) species, which could then be the active polymerization catalyst. The fact that isocyanides are potent reducing agents,[12] however, forced us to consider a pathway wherein nickel(II) is reduced to a less reactive nickel(I) species by isocyanide, and then possibly reoxidized to a more catalytically active nickel(II) species by O_2 (eq 2). Involvement of isocyanide in the redox cycle would also explain the observed oxidation of the monomer in excess O_2.

$$\mathrm{RNi(II)(L)_nX} \xrightarrow{\mathrm{RNC}} [\mathrm{RNi(I)^{\bullet -}(L)_nX} + \mathrm{RNC^{\bullet +}}] \xrightarrow{\mathrm{O_2}} \mathrm{RNi(II)(L)_nX} + \mathrm{RNCO} \quad (2)$$

Direct evidence for the reduction of nickel(II) to nickel(I) by isocyanides under pseudopolymerization conditions was obtained using ESR, cyclic voltammetry, and bulk magnetic susceptibility measurements. ESR spectra of frozen catalyst solutions were recorded at 77 K with and without isocyanide and/or O_2 purging. Both nickel(I) and nickel(III) exhibit characteristic ESR signals,[13] while no signal is usually observed for paramagnetic nickel(II) under these conditions.[13,14] The catalyst solutions without added isocyanide showed no detectable ESR signal, as expected for nickel(II). Immediately upon addition of 10 equiv of *tert*-butyl isocyanide under N_2, a strong axial signal appeared with $g_\perp = 2.120$ and $g_\parallel = 2.012$, characteristic for a nickel(I) $3d^9$ ion with a $(d_{z^2})^1$ ground state.[13] When the solutions were purged with O_2 for 10 min, all the monomer was consumed and the ESR signals disappeared as the catalyst was presumably converted back to nickel(II), consistent with O_2 acting as an oxidizing agent. It is important to note that these O_2 sparges oxidized *all* the isocyanide in the sample to isocyanate and that under true polymerization conditions (*vide infra*) very different results were obtained.

In an effort to determine the extent of the redox behavior indicated by the ESR experiments, bulk magnetic susceptibility measurements were taken on nickel catalyst solutions. In all solvents studied, the catalysts clearly underwent transformation from nickel(II) complexes ($\mu_{\mathrm{eff}} = 2.99\ \mu_B$),[15] to predominantly nickel(I) complexes ($\mu_{\mathrm{eff}} = 2.25\ \mu_B$)[15] upon the addition of 10 equiv of *tert*-butyl isocyanide, and then back to the nickel(II) state ($\mu_{\mathrm{eff}} = 2.94\ \mu_B$) upon extended purging with O_2. Because susceptibility is a bulk property, these results can be qualitatively interpreted to indicate that the *bulk* of the nickel catalyst (as opposed to merely a minute fraction) is converted to the nickel(I) state by isocyanide and then back to the nickel(II) state by *excess* O_2.

To further quantify these redox properties, cyclic voltammograms of catalyst solutions in water were recorded. We found that addition of 10 equiv of isocyanide to a $NiCl_2$ solution in water (under N_2) showed a reversible, one-electron wave with $E_{1/2} = -0.341$ V vs SCE for the Ni(I/II) couple.[16] In the absence of isocyanide, no redox was observed within the solvent window. As expected from our earlier results, exposure of this isocyanide/$NiCl_2$ solution to *excess* O_2 resulted in total oxidation of the isocyanide and the disappearance of the redox couple. These results suggest that coordination of isocyanides to nickel(II) substantially lowers its reduction potential and thereby facilitates the electron-transfer reaction between the nickel center and an isocyanide. It appears that this electron transfer takes place only in the presence of excess (≥10 equiv) isocyanide since well-characterized nickel(II) isocyanide complexes can be isolated.[3a,12b,17]

These results suggest that, under polymerization conditions (i.e., high isocyanide concentrations), nickel(II) catalysts are rapidly reduced to nickel(I) species. Because the polymerization still proceeds, albeit very slowly, under these conditions, nickel(I) salts appear to be mild catalysts. Far more active catalysts can be realized by the controlled introduction of O_2. Yet, since excessive quantities of O_2 were shown to oxidize the catalyst back to the divalent state and produce high yields of isocyanate, the

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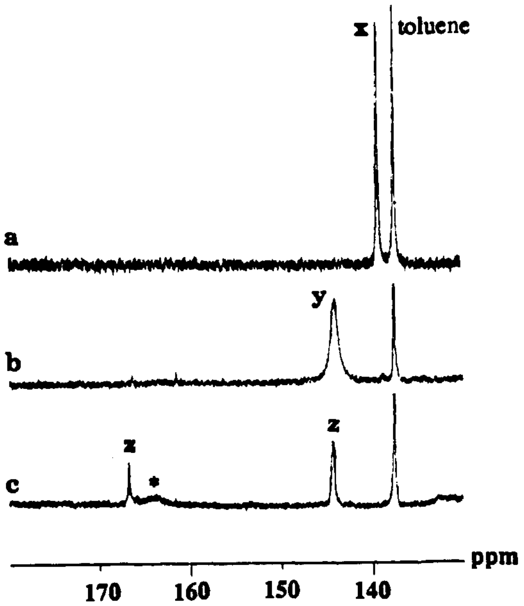
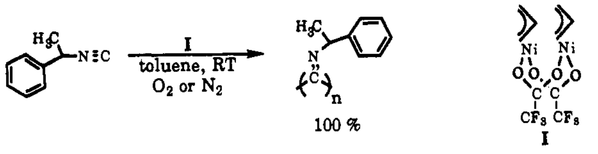


Figure 1. Partial $^{13}C\{^1H\}$ NMR spectra taken after sequential addition of 2, 4, and 6 (**a**, **b**, and **c**, respectively) equiv of 98% ^{13}C-enriched II to I in toluene-d_8 at −60 °C. Assignments: x = $(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)\text{-}^{13}CNR$, y = $(\eta^1\text{-}C_3H_5)Ni(OC(O)CF_3)(^{13}CNR)_2$, z = $[CH_2CHCH_2\text{-}^{13}C(NR)]Ni(OC(O)CF_3)(^{13}CNR)_2$, * = polymer.

role of O_2 in enhancing the polymerization of isocyanides remains unclear from these studies. However, the role of O_2 can be better understood through studies of living isocyanide polymerizations.

Mechanistic Studies: Living Polymerizations. During the course of our studies, we found that the polymerization of 1-phenylethyl isocyanide (**II**) using **I** (eq 3) is a living polymerization under either N_2 or O_2[8] and provides an excellent opportunity to study the pure chain-propagation mechanism in the absence of any side reactions. Our studies showed that initiation of the polymerization proceeds through insertion of an isocyanide into the allyl–nickel bond of **I** to afford an iminoacyl-nickel complex, which then begins the propagation cycle in the polymerization process.[8] In an effort to investigate this initiation mechanism, we synthesized 1-phenylethyl isocyanide labeled with ^{13}C at the isocyanide carbon and observed the reaction of **I** with successive equivalents of this labeled species at low temperature using $^{13}C\{^1H\}$ NMR. Figure 1 shows resonances assignable to a stepwise process in which the first equivalent of isocyanide (per nickel center) has coordinated to dimeric **I**, cleaving the dimer to give the monomeric isocyanide adduct (Figure 1a).[18] Addition of a second equivalent of monomer gave a new resonance that was assigned to a η^1-allyl–bis(isocyanide) complex (Figure 1b). Addition of a third equivalent of isocyanide gave a spectrum assignable to the insertion product (Figure 1c),[19] namely an iminoacyl complex with two coordinated isocyanides. These spectra, along with ^1H and ^{19}F NMR spectra which showed the complete disappearance of **I**, indicated that all of the catalyst molecules were being activated for polymerization upon addition of isocyanide.



(3)

Thus, initial reaction of **I** with isocyanide provides a nickel(II)–iminoacyl complex, yet it remained to be determined whether the nickel(II/I) redox chemistry and the O_2 dependence that was seen above using simple nickel(II) salts occurred in the living polymerization. This question was answered by observation of polymerization reactions: addition of O_2 to a polymerization catalyzed by **I** resulted in an marked visual increase in the polymerization rate. More rigorously, kinetic analysis of the polymerization reaction using **I** gave the rate expressions: propagation rate (v_p) = k_p[catalyst][monomer] under N_2 and v_p = k_p[catalyst] under O_2. Since the rate constants are of the same magnitude (under N_2 (298 K), $k_p = 3.7(1) \times 10^{-2}$ L mol^{-1} s^{-1}; under O_2 (298 K), $k_p = 5.1(1) \times 10^{-2}$ s^{-1}), the oxygen reaction appears faster because of the lack of rate dependence on monomer concentration. Using these rate expressions, we can postulate simple kinetic models for N_2 (eqs 4–8) and O_2 (eqs 9–12) propagation steps which explain the observed rate differences through mechanism changes.

reversible monomer coordination

$$P_nNi(CNR)_xTFA + RNC \xrightleftharpoons[k_{-1}]{k_1} P_nNi(CNR)_{x+1}TFA \tag{4}$$

irreversible monomer insertion

$$P_nNi(CNR)_{x+1}TFA \xrightarrow{k_2} P_{n+1}Ni(CNR)_xTFA \tag{5}$$

$$P_nNi(CNR)_xTFA = P_{n+1}Ni(CNR)_xTFA = cat \tag{6}$$

P_n = polymer chain

$$\frac{-d[RNC]}{dt} = k_1[RNC][cat]\left(1 - \frac{k_{-1}}{k_2 + k_{-1}}\right) \tag{7}$$

if $k_2 >> k_{-1}$ then:

$$\frac{-d[RNC]}{dt} \approx k_1[RNC][cat] \tag{8}$$

reversible monomer insertion

$$P_nNi(CNR)_xTFA \xrightleftharpoons[k_{-1}]{k_1} P_{n+1}Ni(CNR)_{x-1}TFA \tag{9}$$

irreversible monomer coordination

$$P_{n+1}Ni(CNR)_{x-1}TFA + RNC \xrightarrow{k_2} P_{n+1}Ni(CNR)_xTFA \tag{10}$$

using eq 6:

$$\frac{-d[RNC]}{dt} = \frac{k_1k_2[RNC][cat]}{(k_{-1} + k_2[RNC])} \tag{11}$$

if $k_2[RNC] >> k_{-1}$ (high monomer concentrations) then:

$$\frac{-d[RNC]}{dt} \approx k_1[cat] \tag{12}$$

These transition-state differences are more closely examined through measurement of thermodynamic activation parameters (Figure 2). $\Delta H^{\ddagger}(N_2)$ = 6.0(2) kcal/mol and $\Delta S^{\ddagger}(N_2)$ = −60(10) eu from Figure 2 imply a small amount of bond breaking but a significant amount of induced order. We propose this negative and unusually large entropy of activation under N_2 atmosphere is due to "electrostriction" or charge separation developing during the transition state in a nonpolar solvent.[20] This contrasts with $\Delta H^{\ddagger}(O_2)$ = 18.1(1) kcal/mol and $\Delta S^{\ddagger}(O_2)$ = −18(8) eu (Figure 2), where the data imply significant bond breaking and slightly associative behavior in the transition state for polymerization propagation.

We believe the reduction of Ni(II) to Ni(I) by isocyanide causes the charge separation ($Ni(I)^-$ and ^+CNR) in the transition state

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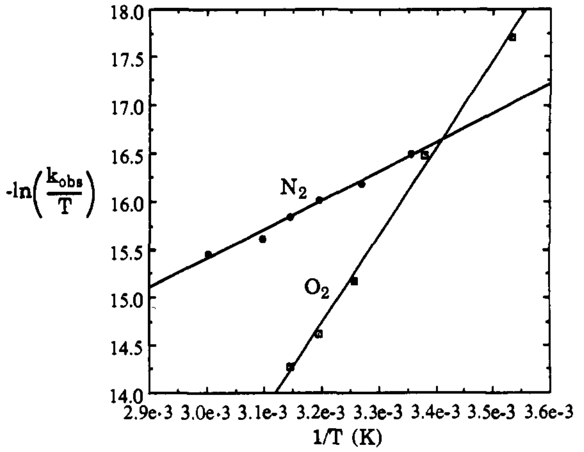
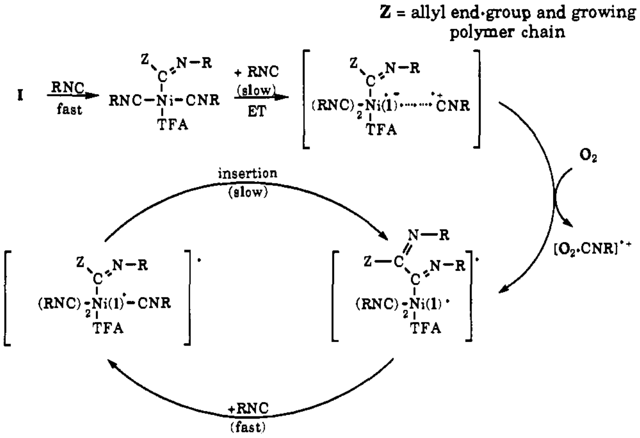
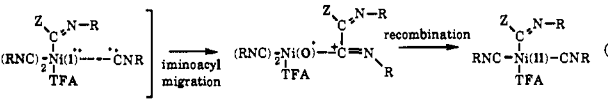


Figure 2. Eyring plots for N_2 and O_2 polymerizations.

Scheme III. Polymerization under Oxygen



under N_2, which is consistent with the rate-determining step having a first-order dependence on the monomer. Conceivably, a cycle of steps consisting of coordination/redox of a monomer followed by migration of the iminoacyl group and then recombination of the charged species (eq 13) can be envisioned for polymerization

 (13)

under N_2. Under O_2, the radical species are assumedly trapped or quenched by the biradical, and the polymerization then proceeds through a reduced nickel(I) species. Under these conditions, the rate-determining step is the migratory insertion of the monomer into the polymer chain, which is consistent with a zero-order dependence on the monomer (Scheme III). Note that O_2 is *not* proposed to act as an oxidizing agent (*vide infra*) yet as a spin trap.

In an effort to study the active catalyst in these living polymerizations, ESR spectra were recorded of the nickel species present under actual polymerization conditions. The spectra acquired for living polymerizations under both N_2 and O_2 at 77 K are given in Figure 3: the signals are due to the presence of nickel(I).[7] Superficially, we recognize that these polymerizations proceed via nickel(I) catalysis, consistent with our previous results. Since the polymerization is living and *all* of the catalyst is active in the polymerization, then these results also illustrate that *all* of the catalyst molecules are involved in this redox cycle.

Note that in Figure 3 the intensities of the two ESR signals differ greatly and that the signal under O_2 is over twice as intense as the signal under N_2 (same concentrations of both monomer and I). These spectra indicate that the amount of nickel(I) is actually *greater* in the presence of a potential oxidizing agent than under an inert atmosphere. Our initial belief of O_2 acting to oxidize nickel(I) to nickel(II) is now unfounded except under forcing, nonpolymerization conditions. Namely, an excess of O_2 can act to oxidize all the isocyanide to isocyanate via nickel, then consequently oxidize the nickel upon depletion of the reducing agent (isocyanide). This is a side reaction separate from polymerization. Under milder conditions (1 atm of O_2), isocyanide reduces nickel(II) to nickel(I), which is then the active polymerization species. O_2 therefore can act as a spin trap and *not* as an oxidizing agent (Scheme III). After reduction of the metal center, oxygen trapping of the resulting isocyanide radical cation, perhaps via a coordination complex intermediate (i.e. a peroxo complex), then leaves a nickel(I) catalyst to propagate the polymerization. Since attempts to trap this isocyanide radical cation using other conventional radical traps (e.g. BHT, TEMPO, nitrones, and nitroso compounds) gave only negative results (rates for these polymerizations with additives were all first order in the monomer under N_2), we feel the isocyanide oxidation product may be bound to nickel, and hence does not exist as a free radical in solution. This hypothesis would explain why only a small spin trap which could easily approach the metal center (i.e. O_2) affects the polymerization process.

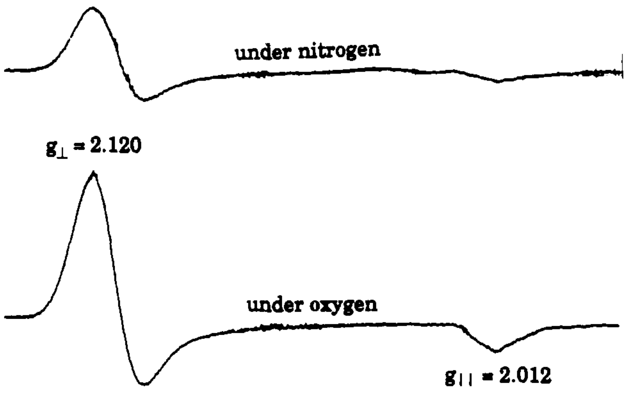


Figure 3. ESR spectra taken at 77 K of polymerizations of (±)-**II** using **I** under nitrogen and oxygen atmospheres in toluene. [RNC] = 1.2 M and [Ni] = 3.9 mM for both.

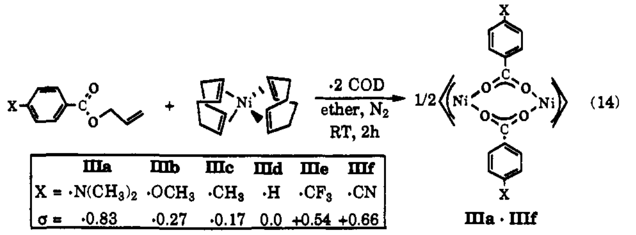
Under N_2 the polymerization is conducted in absence of a potential spin trap and presumably the isocyanide radical cation enters directly into the polymerization cycle. Such interaction means the reduction of the catalyst may be easily reversible, or that the oxidation product of an isocyanide may be intimately involved with the propagation reaction (i.e. within the coordination sphere of the metal center). The latter rationale appears attractive in consideration of the data presented above. We have shown that the living polymerizations under N_2 and O_2 proceed via pathways with different rate-determining steps (i.e. different mechanisms) and that under N_2 a substantial amount of charge separation is developed in the transition state. This charge separation could arise from localization of charges on nickel (anion) and isocyanide (cation), namely oxidation/reduction, which then must occur *throughout* the polymerization. A formal cycle of oxidation/reduction followed by recombination of radicals in the N_2 polymerization would explain the lower concentration of nickel(I) under N_2 in the ESR spectra: only a fraction of the catalyst would exist as nickel(I) in a steady-state concentration, whereas all of the catalyst exists as nickel(I) under O_2. The preceding reactions are summarized in Schemes II and III.

Due to the prevalance of significant charge separation and ionic species in these mechanisms, we decided to probe the electronic structure of the reactive intermediates through sub-

Table I. Molecular Weight and Rate Data for Polymerizations of IV Using III

	O_2 data			N_2 data		
catalyst	$10^{-3}\ k_p$ (s^{-1})	$\overline{M}_n$ poly(IV)	$10^{-4}\ k_{tr}$ (s^{-1})	$10^{-3}\ k_p$ ($M^{-1}\ s^{-1}$)	$\overline{M}_n$ poly(IV)	$10^{-4}\ k_{tr}$ ($M^{-1}\ s^{-1}$)
IIIa	2.74	4820	0.76	0.36	5730	0.08
IIIb	4.11	4330	1.26	0.86	5270	0.22
IIIc	4.76	4910	1.29	1.07	5300	0.27
IIId	5.08	4950	1.37	2.13	5100	0.56
IIIe	7.97	4980	2.13	5.47	5050	1.44
IIIf	8.71	4600	2.52	5.86	4855	1.61

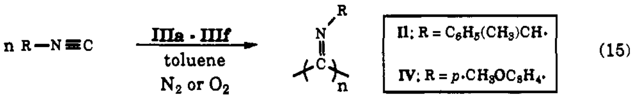
stituent effects.[21] Substituted π-allylnickel benzoates (**IIIa–f**) were found easy to prepare (eq 14), and the compounds themselves



(14)

	IIIa	**IIIb**	**IIIc**	**IIId**	**IIIe**	**IIIf**
X =	·$N(CH_3)_2$	·OCH_3	·CH_3	·H	·CF_3	·CN
σ =	-0.83	-0.27	-0.17	0.0	+0.54	+0.66

as well as the polymerization reactions were tolerant of a wide range of both electron-withdrawing and -donating substituents (eq 15). We subsequently analyzed polymerization propagation



II; R = $C_6H_5(CH_3)CH$·

IV; R = p-$CH_3OC_6H_4$·

(15)

rates (v_p's) for all six catalysts under both N_2 and O_2 atmospheres. The rate expressions for all catalysts under both conditions were identical to those found for **I** with the values of the rate constants (k_p's) being the only differences (Table I). Construction of Hammett plots gave linear fits indicative of an unchanging mechanism throughout the series of catalysts as well as ρ values (298 K) for the propagation reactions (Figure 4).[21] Referring back to Schemes II and III, we would expect a much greater negative charge to build up on the nickel center at the rate-determining step under N_2 than under O_2 (nickel(II) to nickel(I)). Negative charge accumulation would be reflected in a greater positive ρ value, which is what we observe for N_2 polymerization ($\rho = +0.86$). The small positive ρ we observe for the O_2 polymerization ($\rho = +0.34$) is likewise consistent with a lack of charge development in the rate-determining step (nickel(I) goes to nickel(I)) yet has a finite value due to the electron richness of the metal center which is relieved by electron-withdrawing groups.

Chain Transfer. We have so far focused solely on the propagation reaction in isocyanide polymerizations. During the course of these studies, we discovered that not all isocyanide polymerizations initiated by allyl–nickel complexes were living. Another reaction, very important in terms of molecular weight control in polymer synthesis, is chain transfer. Chain transfer is particularly apparent in polymerizations of very sterically encumbered isocyanides (e.g. *tert*-butyl and diphenylmethyl) where only short oligomers can be obtained ($n \leq 50$ and often less then 10).[22] Quantitative yields of polymers of molecular weight significantly lower than predicted by monomer/catalyst stoichiometry indicate that transfer is occurring, yet give no insights into what is actually occurring at the active species. Since the transfer mechanism involves cleavage of a nickel(I)–iminoacyl bond, any plausible mechanism must be consistent with the chemistry of this or related species. Further, since chain transfer occurs both under N_2 and O_2, any proposed mechanism must be in agreement with the cycles in Schemes II and III.

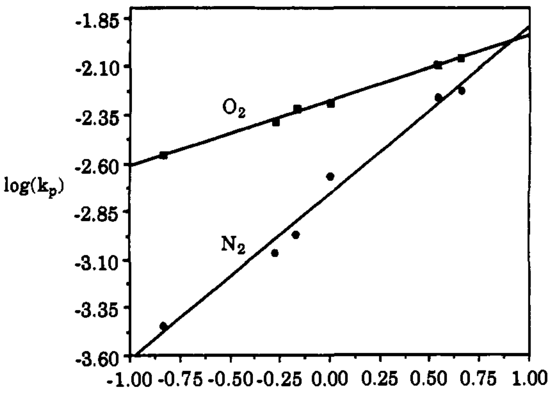


Figure 4. Hammett plots for propagation reactions under N_2 and O_2.

The most probable chain-transfer process has been determined to be homolytic nickel–iminoacyl bond breakage followed by reinitiation of the metal center. There is much literature precedent for homolytic bond fission; in fact, it is the most generally assumed route for organonickel decomposition.[23] In many cases, complexes of the type $RNi(L)_2X$ (where R = alkyl, aryl, acyl; L = PR_3; X = Cl, Br, I) when treated with an excess of a strong donor (e.g. PR_3) react to yield nickel(I) complexes $(L)_3NiX$ and coupled radical products (R–R; decarbonylation is observed when R = acyl).[24] This observation can be rationalized using molecular orbital arguments since coordination of a donor ligand to a d^8 square planar complex effectively populates metal–ligand antibonding orbitals (e′ ($d_{x^2-y^2}$ and d_{xy}) in a trigonal bipyramidal (TBP) geometry).[25] By filling antibonding orbitals, the metal–R bond is weakened and hence is more likely to break. This reaction is fundamentally very similar to the initiation step in our polymerization wherein excess strong donor (isocyanide) reduces the nickel(II) iminoacyl to a nickel(I) iminoacyl. The only difference between the two is that our nickel(I) iminoacyl can propagate (i.e. insert isocyanide monomers) in addition to undergoing bond fission. In the rate-determining step in Scheme II, the iminoacyl group is shown to migrate as a radical to the oxidized isocyanide. If this radical were to instead leave the coordination sphere of the metal, then the polymer chain would cleave and chain transfer would have occurred. In our system, ESR studies have shown that the resting state of the nickel(I) iminoacyl has a TBP structure ($(d_{z^2})^1$ ground state) which could result from a TBP nickel(II) complex.[7] In transforming from nickel(II) to nickel(I), an electron goes into the very strongly antibonding a_1' (d_{z^2}) orbital.[25] For a d^9 system, this will weaken the bond strengths of the apical ligands, which includes the nickel–iminoacyl bond since the complex displays axial symmetry. Hence, the nickel–iminoacyl bond under polymerization conditions (i.e. where the metal is in the +1 oxidation state) should be very weak and prone to homolytic cleavage as well as very fast migratory insertions.

In an effort to support this hypothesis, we devised a system to model the chain-transfer reaction utilizing the nickel–iminoacyl complex, $C_6H_5(Me_3CN{=}C)Ni(PMe_3)_2Br$ (eq 16) (the validity of this compound as a model was verified by kinetic analysis which showed it to have isocyanide polymerization activity

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(21) (a) Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 1. (b) Unger, S. H.; Hansch, C. *Prog. Phys. Org. Chem.* **1976**, *12*, 91. (c) Levitt, L. S.; Widing, H. F. *Prog. Phys. Org. Chem.* **1976**, *12*, 119. (d) Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323.

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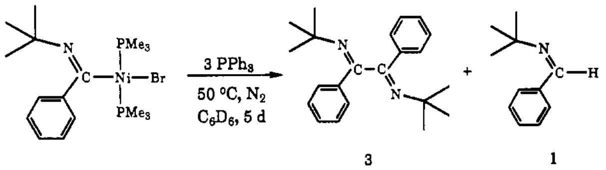
(24) (a) Heimbach, P. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 648. (b) Bartsch, E.; Dinjus, E.; Uhlig, E. *Z. Chem.* **1975**, *15*, 317. (c) Green, M. L. H.; Smith, M. J. *J. Chem. Soc. A* **1971**, 659. (d) Porri, L.; Gallazzi, M. C.; Vitulli, G. *Chem. Commun.* **1967**, 228.

(25) Albright, T. A.; Burdett, J. K.; Whangbo, M. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.



(16)

identical to that of allylnickel bromide complexed with 2 equiv of added trimethylphosphine). Using literature-derived reaction conditions[24] outlined above, we sought to induce homolytic cleavage of the nickel–iminoacyl bond under conditions where chain propagation was eliminated. We were able to spectroscopically identify proton terminated and coupled byproducts from the fission reaction, illustrating that iminoacyls undergo bond fission similar to that of other organic ligands. In addition, we observed no products from the deinsertion of isocyanide (i.e. biphenyl) as expected,[12] as opposed to the deinsertion of carbon monoxide seen in the decomposition of acyl complexes.[26] This result inclines us to propose that chain-transfer reactions in polymerizations do not result in a depolymerization of a chain before it is quenched and that the observed degrees of polymerization are truly those determined by propagation and transfer rates.

The rate of chain transfer and the nature of the rate expression would be valuable in elucidating the mechanism for this process if they could be determined. In polymerizations of this type, where only propagation and transfer are occurring, the degree of polymerization is given by the ratio of the propagation rate (v_p) to the transfer rate (v_{tr}) (eqs 17–18);[27] we have experimentally

under oxygen:

$$\bar{D}_p = \frac{V_p}{V_{tr}} = \frac{k_p[\text{cat}]}{k_{tr}[\text{cat}]} = \frac{k_p}{k_{tr}} \Longrightarrow \boxed{k_{tr}(O_2) = \frac{\bar{D}_p(O_2)}{k_p(O_2)}} \qquad (17)$$

under nitrogen:

$$\bar{D}_p = \frac{V_p}{V_{tr}} = \frac{k_p[\text{cat}][\text{RNC}]}{k_{tr}[\text{cat}][\text{RNC}]} = \frac{k_p}{k_{tr}} \Longrightarrow \boxed{k_{tr}(N_2) = \frac{\bar{D}_p(N_2)}{k_p(N_2)}} \qquad (18)$$

verified this in isocyanide polymerizations where transfer is occurring.[28] Since we have measured propagation rates and since we can measure molecular weights, we were able to experimentally determine transfer rates. These values were determined for **IIIa–f** using *p*-methoxyphenyl isocyanide (**IV**) as a transferring monomer, and Hammett plots are shown in Figure 5. Note that transfer rate constants (k_{tr}'s) were plotted instead of rates (v_{tr}'s). This substitution was made on the assumption that both chain transfer and chain propagation have the same rate expressions with regard to monomer and catalyst dependence. It was assumed that transfer was first order in catalyst based upon the model compound reactivity presented above. The zero- and first-order dependencies on the monomer (O_2 and N_2, respectively) were assumed on the basis of the molecular weight distributions of the polymers obtained: the distributions were monomodal, invariant of initial monomer concentration, and not skewed as would be expected if the transfer rate and propagation rate were different order in the monomer.[28] The Hammond plots show ρ values very similar to those obtained for the propagation reactions ($\rho(N_2) = 0.90$, $\rho(O_2) = 0.33$). These data imply that the steps of propagation and transfer are very electronically similar in nature and probably arise from the same resting intermediates.

Bearing these data in mind, we can begin to construct catalytic cycles for chain transfer under both O_2 and N_2. Under nitrogen, we begin with a nickel(II)–iminoacyl complex (the resting species in the propagation mechanism) which is reduced in the transition state to nickel(I), which then loses the polymer chain as a iminoacyl radical (Scheme IV). This process leads to tris(isocyanide)nickel(I) trifluoroacetate as expected from the phosphine experiments described above. The problem now posed is that tris(isocyanide)nickel(I) trifluoroacetate must be active in the polymerization cycle; if not, this mechanism would be invalid since these reactions would produce chain *termination* and not chain transfer. We decided to test the mechanism by synthesizing intermediates and examining their reactivity. The system was modeled by initially replacing isocyanide ligands with triphenylphosphine and by replacing trifluoroacetate with bromide. We attempted to polymerize racemic **II** in toluene under nitrogen separately with allylnickel(II) bromide, tris(phosphine)nickel(I) bromide, and bis(phosphine)nickel(II) bromide while monitoring the reaction kinetics (Figure 6). From the figure, Ni(II)Br_2 is not an active catalyst as would be expected since it possesses no initiating nucleophilic group.[7] Furthermore, reduction of Ni(II)Br_2 to Ni(I)Br by excess isocyanide does not occur since the complex would have to eliminate a bromine radical rather than an organic radical, which is unprecedented. The only way Ni(II)Br_2 can enter the polymerization cycle is through addition of a nucleophilic initiator.

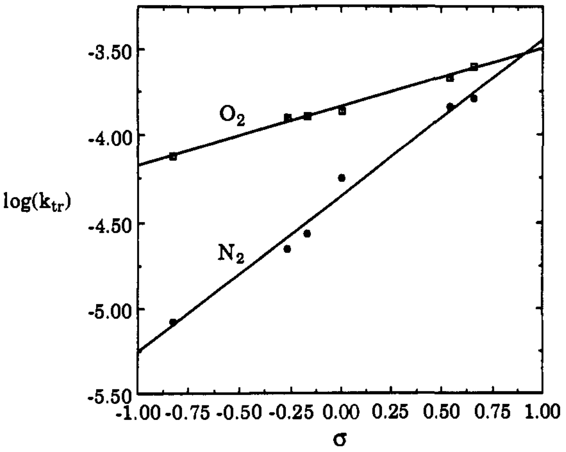
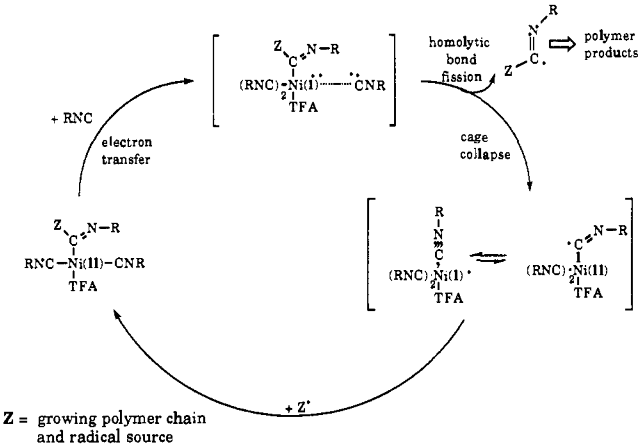


Figure 5. Hammett plots for chain-transfer reactions under N_2 and O_2.

Scheme IV. Chain Transfer under Nitrogen



The figure also shows allylnickel(II) bromide to be an active catalyst, which is expected since this compound is analogous to **I**. What we observe for the nickel(I) salt is an induction period followed by high polymerization activity which nearly matches that of the allyl complex. This result is in good accord with our proposed mechanism in that the tris(isocyanide)nickel(I) salt (formed *in situ* from the phosphine complex) must react with some radical to be able to form a nickel(II) iminoacyl (i.e. the reaction of a radical (R•) with a nickel(I) species (Ni(I)X) formally gives a nickel(II) complex bearing an initiator group

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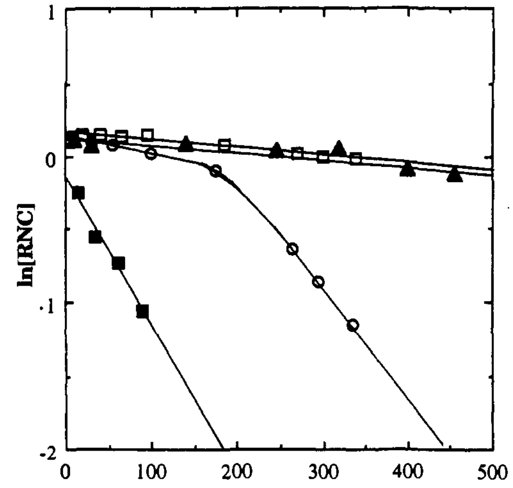
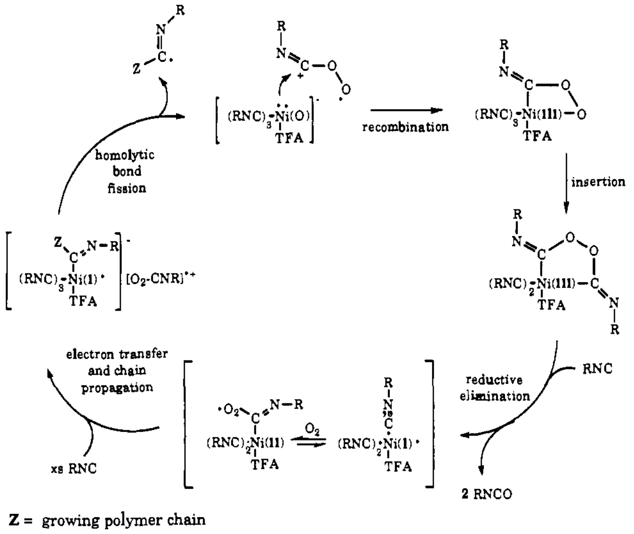


Figure 6. Rates of disappearance of (±)-II versus time under nitrogen for different catalysts: (allyl)Ni(II)Br + 3PPh_3 (black squares), $(PPh_3)_3$-Ni(I)Br (white circles), $(PPh_3)_3$Ni(I)Br + BHT (black triangles), and $(PPh_3)_2$Ni(II)Br_2 + PPh_3 (white squares). All have identical initial concentrations of nickel and monomer.

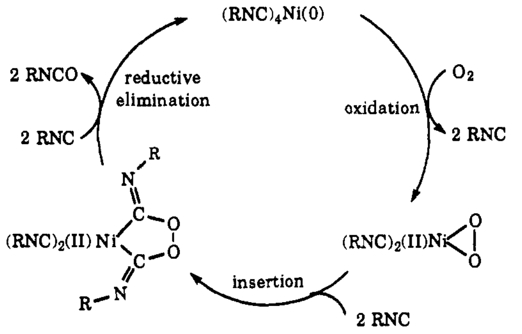
Scheme V. Chain transfer under Oxygen



(RNi(II)X), which is analogous to I and can start polymerization) (Scheme IV). Presumably the induction period is the time required to abstract/release radicals which start a chain reaction to initiate the nickel(I) salts (as shown in Figure 6, addition of a radical trap (BHT) to the nickel(I) complex inhibits polymerization activity). Once initiated, these salts enter the chain-transfer-propagation cycle and proceed to make the polymer at the same rate as the allyl catalyst. Note that, under polymerization conditions using **I**, the induction period would presumably disappear since the nickel(I) salts are formed after chain scission (initiation) and the free radicals necessary for propagation would be present in the reaction mixture.

Under oxygen the resting state of the catalyst (i.e. the complex preceeding the rate-determining step) is a nickel(I) species. This complex can either undergo a migratory insertion reaction of the iminoacyl or can lose this group by homolytic cleavage of the bond with nickel. The latter route (chain transfer) produces a "dead" polymer chain and a nickel(0)-isocyanide complex (Scheme V). This electron-rich complex can then react with the isocyanide oxidation product in a manner very similar to the proposed mechanism of isocyanide oxidation via nickel (Scheme VI).[29] This overall net reaction eliminates 2 equiv of isocyanate and leaves the same tris(isocyanide)nickel(I) trifluoroacetate complex we proposed was formed under inert atmosphere. Now, however, there is the biradical O_2 present which can react with the nickel(I) salt as a radical initiator to regenerate the active species (Scheme V). If we, now under oxygen, attempt to polymerize 1-phenylethyl isocyanide separately with allylnickel(II) bromide, tris(phosphine)nickel(I) bromide, and bis(phosphine)nickel(II) bromide while monitoring the reaction kinetics, we observe (Figure 7) results similar to those for nitrogen polymerization. The one exception is that tris(phosphine)nickel(I) bromide now shows no induction period and shows activity identical to that of allylnickel(II) bromide. This follows from the discussion above in that now that we have a radical source (oxygen); the nickel(I) salt undergoes immediate initiation into the catalytic cycle.

Scheme VI. Oxidation of RNC through Nickel(0) Catalysis



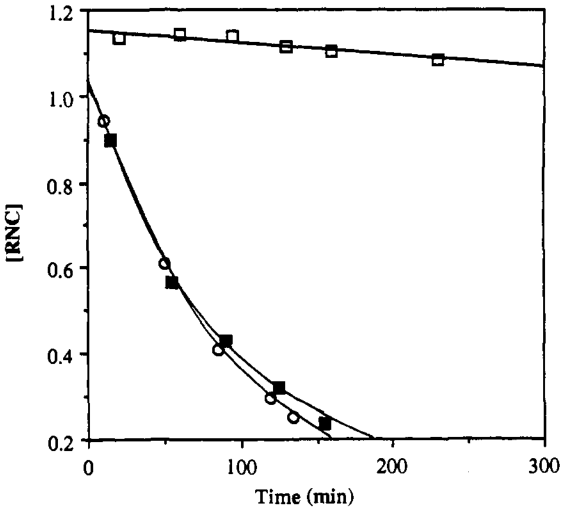


Figure 7. Rates of disappearance of (±)-II versus time under oxygen for different catalysts: (allyl)Ni(II)Br + 3PPh_3 (black squares), $(PPh_3)_3$-Ni(I)Br (white circles), and $(PPh_3)_2$Ni(II)Br_2 + PPh_3 (white squares). All have identical initial concentrations of nickel and monomer.

Another possible event not discussed above is that of the nickel(I) salt disproportionating under the influence of excess isocyanide to bis(isocyanide)nickel(II) bis(bromide) and tetrakis(isocyanide)nickel(0). This reaction of nickel(I) salts has been proposed in a few literature reactions involving decomposition of organonickel(II) complexes in presence of phosphines.[30] Under these conditions, the nickel(II) salt formed would be inert as we had determined above. Thus the active part of the mixture would have to be the nickel(0) complex. To test this possibility, we attempted a polymerization of 1-phenylethyl isocyanide using tetrakis(triphenylphosphine)nickel(0) under O_2. We observed a very rapid disappearance of the monomer comparable to rates observed for using allylnickel bromide and tris(phosphine)nickel(I) bromide; however, the monomer was not converted to the polymer but to the corresponding isocyanate, as determined by

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(30) Carmona, E.; Marin, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757.

IR spectroscopy. This type of behavior has been observed previously and is believed to proceed through a nickel peroxide complex (Scheme VI).[29]

These results were reminiscent of our earlier studies wherein nickel salts were found to oxidize rather than polymerize isocyanides under forcing conditions. In reexamining our experiments on the nickel(I) complex under O_2, we found that nearly all of the monomer was polymerized to the high polymer, indicating that nickel(I) is active in the polymerization cycle, although some oxidized product (ca. 5%) was observed. Furthermore, upon investigation of polymerization data for a variety of monomers using catalyst **I** under O_2, we discovered that all monomers which were observed to undergo chain transfer produced measurable quantities of the corresponding isocyanate under polymerization conditions.[28] Therefore, it appears that a general consequence of chain transfer in nickel-catalyzed isocyanide polymerizations under O_2 is the formation of some isocyanate byproduct which may be formed from the processes in Scheme V or through the irreversible formation of some nickel(0) complex(es) which catalyzes the oxidation of isocyanides.

Relevance of Results to Polymer Synthesis. As an ultimate goal, we desire a polymerization system(s) which would allow preparation of polymers of defined molecular weights and narrow polydispersities for all polyisocyanides regardless of substituent. From the results detailed above, we see chain transfer via homolytic cleavage of the chain end as a major obstacle. The close similarities between the propagation and transfer steps further complicate the problem: if we slow down the transfer reaction, then we also show the propagation reaction. An obvious solution to the problem of a weak metal–iminoacyl bond would be to change the metal in favor of a stronger interaction. Work has been done in this area by going down the periodic column and using palladium compounds to polymerize aryl isocyanides.[3a,31] Palladium, being harder to reduce than nickel, remains in the divalent oxidation state throughout the polymerization and consequently also remains diamagnetic. These polymerization systems have been reported to produce living poly(aryl isocyanides) and thus retain the palladium as a polymer endgroup.[32] This is to be expected, since, in the case of nickel, the reduced metal ion would be expected to have very labile ligands, whereas the ligands would be expected to be far less labile in an unperturbed complex. The disadvantage of palladium catalysis is that it is very slow relative to that of nickel: the stronger bonds and decreased lability, while providing control, also reduce activity.[31]

Another alternative to exchanging the metal is the design of a more sophisticated catalyst system. We have begun preliminary work in this area using cyanide as a reactivity-controlling ligand. Addition of 1, 2, or 3 equiv of CN^- (as a tetraalkylammonium salt) per nickel center in **I** results in the formation of the stable anionic cyano adducts. We have previously shown that addition of 3 equiv of cyanide per nickel to polymerization systems completely inhibits polymer formation since the anionic CN^- proves to be a much stronger ligand than neutral isocyanides and saturates the nickel centers.[22] Addition of fewer equivalents of CN^- leaves coordination positions open so polymerization can occur, yet effectively binds some of the coordination sphere of the metal. Through manipulation of the coordination sphere of the nickel catalyst, we hoped to control its reactivity and possibly control the polymerization reactions.

Polymerization of *n*-hexyl isocyanide using **I** under standard conditions yielded only a black tarry material of low molecular weight (*ca* 3500). Examination of the literature revealed that all other attempts to produce poly(*n*-hexyl isocyanide), including glass–acid initiators, yield the same deep brown products.[33] However, addition of 2 equiv of CN^- per nickel center in **I** before addition of the monomer gave a polymerization mixture which remained pale yellow and, after work up, gave a tan polymer of much higher molecular weight (*ca.* 20 000) in high yield (*ca.* 80%). In toluene solvent, the molecular weight was found to be invariant with monomer to catalyst stoichiometry, yet in acetonitrile the molecular weight of the polymer could be controlled to a limited extent by varying stoichiometries (monomer:catalyst = 593:1, $\overline{M}_n$ = 36 270; monomer:catalyst = 296:1, $\overline{M}_n$ = 16 170).

Presumably, the permanent replacement of isocyanide monomers with less sterically demanding cyanide ligands on the coordination sphere of the metal generates an active center with less overall steric hindrance where the polymer chain is attached to nickel. This steric freedom could relieve strain on the nickel–iminoacyl bond, strengthening the interaction and decreasing the potential for cleavage of the bond (in other words, chain transfer). By understanding the mechanisms in polymerization processes, we are confident that a great deal of progress can be attained in controlling polymer synthesis.

Experimental Section

The synthesis and subsequent manipulations of the complexes and polymers described below were conducted under dinitrogen atmosphere with the rigorous exclusion of air and water (except where noted) by usng Schlenk line and glovebox (Vacuum Atmospheres HE 553 Dri Lab with attached HE 493 Dri Train) techniques. *Caution*! Isocyanides exhibit a characteristic sickening stench even at very low concentrations. All manipulations involving isocyanides should be performed in a fume hood and contaminated glassware rinsed with or soaked in a dilute solution of $NiCl_2$ in methanol.

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Toluene and hexane were distilled from sodium benzophenone ketyl under dinitrogen and were stored under dinitrogen before use. Diethyl ether, THF-d_8, C_6D_6, and toluene-d_8 were vacuum transferred from sodium benzophenone ketyl. *tert*-Butyl isocyanide and acetonitrile were vacuum transferred from CaH_2, and $CDCl_3$ was vacuum transferred from P_2O_5. Anhydrous $NiCl_2$ was prepared by drying the hydrate at 10^{-5} Torr. Greater than 98% ^{13}C(carbonyl) ethyl formate was purchased from ICON Chemical Co. and used as received. Ni(1,5-cyclooctadiene)$_2$ was obtained from Strem Chemical Co. and used as received. Allylnickel trifluoroacetate (**I**),[34] allylnickel bromide,[35] tris(triphenylphosphine)nickel(I) bromide,[24a] *p*-methoxyphenyl isocyanide (**IV**),[36] *n*-hexyl isocyanide,[36] and 1-phenylethyl isocyanide (*R*/*S*-**II**)[36] were prepared according to literature methods.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer Model 1605 FTIR spectrophotometer and are uncalibrated. ^1H, ^{19}F, ^{31}P {^1H}, and ^{13}C {^1H} NMR spectra were recorded using either a Bruker AM-400 or AM-500 spectrometer, both equipped with Oxford Instruments magnets. For low-temperature experiments, the sample was cooled to the desired temperature in the NMR probe using N_2(l). The sample was then ejected, *R*/*S*-**II** was added via syringe, and the sample was quickly lowered back into the probe and the NMR spectrum acquired after thermal equilibration. ^1H spectra were referenced by assigning the residual solvent protons as follows: C_6D_6, 7.15 ppm; THF-d_8, 1.78 ppm (β-methylene); toluene-d_8, 2.10 ppm (methyl); $CDCl_3$, 7.26 ppm. ^{19}F spectra were referenced at –60.0 ppm to external $C_6H_5CF_3$. ^{31}P {^1H} spectra were referenced at 0.0 ppm to external H_3PO_4. ^{13}C{^1H} spectra were referenced by assigning the solvent carbons as follows: C_6D_6, 128 ppm; toluene-d_8, 20.5 ppm (methyl); $CDCl_3$, 77 ppm. Magnetic susceptibility measurements were performed using the Evans method[37] on either a Bruker AM-400 or AM-500 NMR spectrometer, and diamagnetic corrections were made using Pascal's constants.[38] ESR spectra were recorded using a Bruker ER 200D-SRC X-band spectrometer with the sample cooled to 77 K by immersion of the sample into a liquid dinitrogen-filled Dewar

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[39] Carmona, E.; Paneque, M.; Poveda, M. L. *Polyhedron* **1989**, *8*, 285.

flask in the sample compartment. The *g* values were referenced to external 2,2-diphenyl-1-picrylhydrazyl (DPPH) at $g = 2.0037$. Cyclic voltammograms were obtained using a Au disc working electrode, Pt wire counter electrode, and Ag wire/$AgNO_3$ reference electrode on a EG&G Princeton Applied Research model 173 potentiostat equipped with a model 178 electrometer probe. The CV spectra were recorded on a Houston Instruments 200 XY recorder. Potassium ferrocyanide trihydrate (water [$E_{1/2} = +0.28$ V vs Ag wire, $E_{pc} - E_{pa} = 200$ mV, scan rate = 100 mV/s]) and ferrocene (acetonitrile [$E_{1/2} = +0.066$ V vs Ag wire, $E_{pc} - E_{pa} = 300$ mV, scan rate = 200 mV/s]) were used as internal references, and potentials were then referenced back to SCE. Gel permeation chromatography (GPC) was performed, using a THF eluent, on a Hewlett/Packard 1050 series liquid chromatograph pump equipped with a HP model 1047 refractive index detector and HP model 3396A integrator. Separations were effected by 10^5-, 10^4-, 10^3-, and 500-Å Waters Ultrastryagel columns, and molecular weights were calibrated relative to polystyrene standards. Elemental analyses were performed by the University of California, Berkeley, microanalytical laboratory. Satisfactory analyses were obtained for all polymer samples prepared.

***trans*-$\mathbf{NiCl_2[CNC(CH_3)_3]_2}$.** In the glovebox, $NiCl_2$ (115 mg, 0.890 mmol) was added to a 150-mL Schlenk flask containing 60 mL of toluene. The flask was then capped with a septum, removed from the glovebox, and brought under dinitrogen atmosphere on a Schlenk line. To this suspension was added *tert*-butyl isocyanide (0.200 mL, 1.77 mmol), and the mixture was allowed to stir overnight (20 h). The red solution was filtered, and the solvent was removed under vacuum to leave a green powder. This powder was washed with hexane (25 mL) to leave the product as a bright yellow powder (187 mg, 71%). Attempts to recrystallize this product led only to its decomposition. IR (toluene): 2220 cm^{-1} (ν(CN), vs). ^1H NMR (C_6D_6): δ 0.61 (s, $-\mathrm{CNC(C}H_3)_3$). Anal. Calcd for $NiC_{10}H_{18}N_2Cl_2$: C, 40.54%; H, 6.14%; N, 9.46%. Found: C, 39.44%; H, 5.21%; N, 9.71%. The single ν(CN) stretch in the IR spectrum and the compound's diamagnetic behavior permitted assignment as the *trans* square planar complex.

Oxidation of Isocyanide to Isocyanate. *tert*-Butyl isocyanide (0.050 mL, 0.44 mmol) was added to a solution of $NiCl_2[CNC(CH_3)_3]_2$ (3 mg, 0.01 mmol) in (THF-d_8): (0.5 mL) under dinitrogen, and the IR and ^1H NMR spectra were recorded. IR 2135 cm^{-1} (ν(CN), vs). ^1H NMR (THF-d_8): δ 1.55 (t, $\mathrm{CNC(C}H_3)_3$). This solution was purged with dioxygen for 2 h at 0 °C by bubbling the gas through the solution using a long needle with the NMR tube immersed in an ice/water bath, during which the orange solution turned pale green. IR and ^1H NMR analysis revealed the solution to contain *tert*-butyl isocyanate (quantitative yield by NMR). IR(THF-d_8): 2259 cm^{-1} (ν(NCO), vs). ^1H NMR (THF-d_8): δ 1.68 (s, $\mathrm{OCNC(C}H_3)_3$). The same experiment, performed without the nickel catalyst, gave only starting material and no detectable quantities of the isocyanate (by NMR).

(±)-$\mathbf{C_6H_5(CH_3)CHN^{13}C}$. ^{13}C ethyl formate was reacted with (±)-1-phenylethylamine to give 1-phenylethyl(^{13}C)formamide in quantitative yield. This formamide was then dehydrated using the phosgene method[37] to leave, after distillation (40 °C/0.05 Torr), pure 1-phenylethyl isocyanide labeled with ^{13}C at the isocyanide carbon (80% yield). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 159.9 (s, $\mathit{C}\mathrm{NCH(CH_3)C_6H_5}$).

1,4-$\mathbf{CH_2CHCH_2O_2CC_6H_4CN}$ (APCB). To a 25-mL round-bottom flask containing 1,4-$NCC_6H_4C(O)Cl$ (0.890 g, 5.39 mmol) in CH_2Cl_2 (10 mL) was added pyridine (0.436 mL, 5.39 mmol) and allyl alcohol (0.366 mL, 5.39 mmol). The reaction was stirred under nitrogen atmosphere for 2 h whereupon the contents were washed with water (2 × 10 mL), dried with $MgSO_4$, and then concentrated by removal of the solvent *in vacuo* to leave a white oily solid. Extraction of this solid with dry ethyl ether and removal of the solvent gave the product as a white solid (0.66 g, 66%). IR (neat): 2320 cm^{-1} (ν(CN), vs), 1728 cm^{-1} (ν(CO), vs). ^1H NMR ($CDCl_3$): δ 8.15 (d, Ar*H*, 2H), 7.75 (d, Ar*H*, 2H), 6.02 (ddt, $-\mathrm{OCH_2C}H\mathrm{CH_2}$, 1H), 5.42 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 5.32 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 4.86 (d, $-\mathrm{OC}H_2\mathrm{CHCH_2}$, 2H).

1,4-$\mathbf{CH_2CHCH_2O_2CC_6H_4CF_3}$ (APTFB). To a 25-mL round-bottom flask containing 1,4-$F_3CC_6H_4C(O)Cl$ (0.800 mL, 5.39 mmol) in CH_2Cl_2 (10 mL) were added pyridine (0.436 mL, 5.39 mmol) and allyl alcohol (0.366 mL, 5.39 mmol). The reaction was stirred under nitrogen atmosphere for 2 h whereupon the contents were washed with water (2 × 10 mL), dried with $MgSO_4$, and then concentrated by removal of the solvent *in vacuo* to leave a white oily solid. Extraction of this solid with dry hexanes/ethyl ether (1:1) and removal of the solvent gave the product as a white solid (0.78 g, 68%). IR (neat): 1728 cm^{-1} (ν(CO), vs). ^1H NMR ($CDCl_3$): δ 8.17 (d, Ar*H*, 2H), 7.71 (d, Ar*H*, 2H), 6.04 (ddt, $-\mathrm{OCH_2C}H\mathrm{CH_2}$, 1H), 5.42 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 5.32 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 4.86 (d, $-\mathrm{OC}H_2\mathrm{CHCH_2}$, 2H). ^{19}F NMR ($CDCl_3$): δ −62.9 (s, $-CF_3$).

$\mathbf{CH_2CHCH_2O_2CC_6H_5}$ (AB). To a 25-mL round-bottom flask containing $C_6H_5C(O)Cl$ (0.626 mL, 5.39 mmol) in CH_2Cl_2 (10 mL) were added pyridine (0.436 mL, 5.39 mmol) and allyl alcohol (0.366 mL, 5.39 mmol). The reaction was stirred under nitrogen atmosphere for 2 h whereupon the contents were washed with water (2 × 10 mL), dried with $MgSO_4$, and then concentrated by removal of the solvent *in vacuo* to leave a white oily solid. Extraction of this solid with dry hexanes/ethyl ether (1:1) and removal of the solvent gave the product as a white solid (0.68 g, 78%). IR (neat): 1720 cm^{-1} (ν(CO), vs). ^1H NMR ($CDCl_3$): δ 8.06 (d, Ar*H*, 2H), 7.67 (t, Ar*H*, 1H), 7.45 (t, Ar*H*, 2H), 6.04 (ddt, $-\mathrm{OCH_2C}H\mathrm{CH_2}$, 1H), 5.42 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 5.29 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 4.83 (d, $-\mathrm{OC}H_2\mathrm{CHCH_2}$, 2H).

1,4-$\mathbf{CH_2CHCH_2O_2CC_6H_4CH_3}$ (APMB). To a 25-mL round-bottom flask containing 1,4-$H_3CC_6H_4C(O)Cl$ (0.713 mL, 5.39 mmol) in CH_2Cl_2 (10 mL) were added pyridine (0.436 mL, 5.39 mmol) and allyl alcohol (0.366 mL, 5.39 mmol). The reaction was stirred under nitrogen atmosphere for 2 h whereupon the contents were washed with water (2 × 10 mL), dried with $MgSO_4$, and then concentrated by removal of the solvent *in vacuo* to leave a milky oil. Extraction of this oil with dry hexanes/ethyl ether (1:1) and removal of the solvent gave the product as a colorless oil (0.67 g, 70%). IR (neat): 1712 cm^{-1} (ν(CO), vs). ^1H NMR ($CDCl_3$): δ 7.96 (d, Ar*H*, 2H), 7.25 (d, Ar*H*, 2H), 6.03 (ddt, $-\mathrm{OCH_2C}H\mathrm{CH_2}$, 1H), 5.41 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 5.28 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 4.81 (d, $-\mathrm{OC}H_2\mathrm{CHCH_2}$, 2H), 2.41 (s, $-\mathrm{C}H_3$, 3H).

1,4-$\mathbf{CH_2CHCH_2O_2CC_6H_4OCH_3}$ (APMOB). To a 25-mL round-bottom flask containing 1,4-$H_3COC_6H_4C(O)Cl$ (58% solution in toluene) (1.49 mL, 5.39 mmol) in CH_2Cl_2 (10 mL) were added pyridine (0.436 mL, 5.39 mmol) and allyl alcohol (0.366 mL, 5.39 mmol). The reaction was stirred under nitrogen atmosphere for 2 h whereupon the contents were washed with water (2 × 10 mL), dried with $MgSO_4$, and then concentrated by removal of the solvent *in vacuo* to leave a milky oil. Extraction of this oil with dry hexanes/ethyl ether (1:1) and removal of the solvent gave the product as a colorless oil (0.76 g, 73%). IR (neat): 1711 cm^{-1} (ν(CO), vs). ^1H NMR ($CDCl_3$): δ 8.02 (d, Ar*H*, 2H), 6.95 (d, Ar*H*, 2H), 6.03 (ddt, $-\mathrm{OCH_2C}H\mathrm{CH_2}$, 1H), 5.40 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 5.27 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 4.80 (d, $-\mathrm{OC}H_2\mathrm{CHCH_2}$, 2H), 3.86 (s, $-\mathrm{OC}H_3$, 3H).

1,4-$\mathbf{CH_2CHCH_2O_2CC_6H_4N(CH_3)_2}$ (APMAB). To a 25-mL round-bottom flask containing 1,4-$(H_3C)_2NC_6H_4C(O)OH$ (1.00 g, 6.05 mmol) in CH_2Cl_2 (10 mL) was added oxalyl chloride (0.528 mL, 6.05 mmol) whereupon the mixture instantly began evolving gas. The gray suspension was stirred until the evolution stopped (5 min), and to the resulting green suspension were added pyridine (0.500 mL, 6.18 mmol) and allyl alcohol (0.450 mL, 6.63 mmol). The resulting green solution was stirred under nitrogen atmosphere for 2 h whereupon the contents were washed with water (2 × 10 mL), dried with $MgSO_4$, and then concentrated by removal of the solvent *in vacuo* to leave a pale blue oil. Extraction of this oil with dry hexanes/ethyl ether (1:1) and removal of the solvent gave the product as a white oily solid (0.75 g, 60%). IR (neat): 1695 cm^{-1} (ν(CO), vs). ^1H NMR ($CDCl_3$): δ 7.94 (d, Ar*H*, 2H), 6.65 (d, Ar*H*, 2H), 6.02 (ddt, $-\mathrm{OCH_2C}H\mathrm{CH_2}$, 1H), 5.38 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 5.25 (dd, $-\mathrm{OCH_2CHC}H_2$, 1H), 4.77 (d, $-\mathrm{OC}H_2\mathrm{CHCH_2}$, 2H), 3.04 (s, $-\mathrm{N(C}H_3)_2$, 6H).

$\mathbf{[(\eta^3\text{-}C_3H_5)Ni(O_2CC_6H_4(CH_3)_2)]_2}$ (IIIa). In the drybox, to a 10-mL round-bottom flask containing a stirbar and Ni(1,5-cyclooctadiene)$_2$ (134 mg, 0.487 mmol) in ethyl ether (5 mL) was added a solution of APMAB (100 mg, 0.487 mmol) in ethyl ether (2.5 mL). The mixture instantly began to turn orange, and within a minute, a red/orange precipitate began to form. The reaction was let stir for 1 h whereupon the solvent was removed *in vacuo* to leave a reddish oily solid which was washed with hexanes and then extracted with CH_2Cl_2 to give a red solution. This solution was filtered to remove any metallic nickel, and then the solvent was removed to leave the product as a red powder (55 mg, 43%). IR ($CHCl_3$): 1604 cm^{-1} (ν(CO), vs). ^1H NMR ($CDCl_3$): δ 7.71 (br d, Ar*H*, 2H), 6.51 (br d, Ar*H*, 2H), 6.00 (br m, $\eta^3\text{-}\mathrm{H_aH_bCC(}H_c\mathrm{)CH_bH_a{-}Ni}$, 1 H), 3.03 (m, $\eta^3\text{-}\mathrm{H_a}H_b\mathrm{CC(H_c)C}H_b\mathrm{H_a{-}Ni}$, 2H), 2.93 (s, $-\mathrm{N(C}H_3)_2$, 6H), 2.49 (m, $\eta^3\text{-}H_a\mathrm{H_bCC(H_c)CH_b}H_a\mathrm{{-}Ni}$, 2H). Anal. Calcd for $Ni_2C_{24}H_{30}N_2O_4$: C, 54.60%; H, 5.74%; N, 5.30%. Found: C, 54.64%; H, 5.60%; N, 5.04%.

$\mathbf{[(\eta^3\text{-}C_3H_5)Ni(O_2CC_6H_4OCH_3)]_2}$ (IIIb). In the drybox, to a 10-mL round-bottom flask containing a stirbar and Ni(1,5-cyclooctadiene)$_2$ (71.5 mg, 0.260 mmol) in ethyl ether (4 mL) was added a solution of APMOB (50.0 mg, 0.260 mmol) in ethyl ether (2.5 mL). The mixture instantly began to turn orange and within a minute became a red/orange solution. The reaction was let stir for 1 h whereupon the solution was filtered to remove any metallic nickel, and then the solvent was removed *in vacuo* to leave a reddish oily solid. This solid was washed with cold (–40 °C) hexanes and then dried to leave the product as a red/orange powder (50 mg, 77%). IR ($CHCl_3$): 1603 cm^{-1} (ν(CO), vs). ^{1}H NMR ($CDCl_3$): δ 7.77 (br d, Ar*H*, 2H), 6.76 (br d, Ar*H*, 2H), 6.02 (br m, η^3-$\mathrm{H_aH_bCC}(H_c)\mathrm{CH_bH_a}$–Ni, 1H), 3.77 (s, –O$\mathrm{C}H_3$, 3H), 3.05 (m, η^3-$\mathrm{H_a}H_b\mathrm{CC(H_c)C}H_b\mathrm{H_a}$–Ni, 2H), 2.55 (m, η^3-$H_a\mathrm{H_bCC(H_c)CH_b}H_a$–Ni, 2H). Anal. Calcd for $Ni_2C_{22}H_{24}O_6$: C, 52.65%; H, 4.83%. Found: C, 52.76%; H, 4.61%; N, 0.00%.

$[(\eta^3\text{-}C_3H_5)Ni(O_2CC_6H_4CH_3)]_2$ (IIIc). IIIc was prepared by following a procedure analogous to that of **IIIb**. Yield: 52 mg, 78%. IR ($CHCl_3$): 1603 cm^{-1} (ν(CO), vs). ^{1}H NMR ($CDCl_3$): δ 7.71 (br d, Ar*H*, 2H), 7.05 (br d, Ar*H*, 2H), 6.10 (br m, η^3-$\mathrm{H_aH_bCC}(H_c)\mathrm{CH_bH_a}$–Ni, 1H), 3.06 (m, η^3-$\mathrm{H_a}H_b\mathrm{CC(H_c)C}H_b\mathrm{H_a}$–Ni, 2H), 2.57 (m, η^3-$H_a\mathrm{H_bCC(H_c)CH_b}H_a$–Ni, 2H), 2.29 (s, –C$H_3$, 3H). Anal. Calcd for $Ni_2C_{22}H_{24}O_4$: C, 56.24%; H, 5.16%. Found: C, 56.33%; H, 5.00%; N, 0.00%.

$[(\eta^3\text{-}C_3H_5)Ni(O_2CC_6H_5)]_2$ (IIId). IIId was prepared by following a procedure analogous to that of **IIIb**. Yield: 58 mg, 85%. IR ($CHCl_3$): 1603 cm^{-1} (ν(CO), vs). ^{1}H NMR ($CDCl_3$): δ 7.83 (br d, Ar*H*, 2H), 7.53 (br m, Ar*H*, 1H), 7.36 (br d, Ar*H*, 2h), 6.05 (br m, η^3-$\mathrm{H_aH_bCC}(H_c)\mathrm{CH_bH_a}$–Ni, 1H), 3.10 (m, η^3-$\mathrm{H_a}H_b\mathrm{CC(Hc)C}H_b\mathrm{H_a}$–Ni, 2H), 2.56 (m, η^3-$H_a\mathrm{H_bCC(H_c)CH_b}H_a$–Ni, 2H). Anal. Calcd for $Ni_2C_{20}H_{20}O_4$: C, 54.62%; H, 4.59%. Found: C, 54.23%; H, 4.23%; N, 0.00%.

$[(\eta^3\text{-}C_3H_5)Ni(O_2CC_6H_4CF_3)]_2$ (IIIe). IIIe was prepared by following a procedure analogous to that of **IIIb**. Yield: 63 mg, 98%. IR ($CHCl_3$): 1604 cm^{-1} (ν(CO), vs). ^{1}H NMR ($CDCl_3$): δ 7.92 (br d, Ar*H*, 2H), 7.51 (br d, Ar*H*, 2H), 6.30 (br m, η^3-$\mathrm{H_aH_bCC}(H_c)\mathrm{CH_bH_a}$–Ni, 1H), 3.12 (m, η^3-$\mathrm{H_a}H_b\mathrm{CC(H_c)C}H_b\mathrm{H_a}$–Ni, 2H), 2.52 (m, η^3-$H_a\mathrm{H_bCC(H_c)CH_b}H_a$–Ni, 2H). ^{19}F NMR ($CDCl_3$): δ –72.6 (s, –CF_3). Anal. Calcd for $Ni_2C_{22}H_{18}O_4F_6$: C, 48.40%; H, 3.33%. Found: C, 48.67%; H, 3.03%; N, 0.00%.

$[(\eta^3\text{-}C_3H_5)Ni(O_2CC_6H_4CN)]_2$ (IIIf). IIIf was prepared by following a procedure analogous to that of **IIIa**. Yield: 42 mg, 43%. IR ($CHCl_3$): 2185 (ν(CN), vs), 1604 cm^{-1} (ν(CO), vs). ^{1}H NMR ($CDCl_3$): δ 7.90 (br d, Ar*H*, 2H), 7.57 (br d, Ar*H*, 2H), 6.18 (br m, η^3-$\mathrm{H_aH_bCC}(H_c)\mathrm{CH_bH_a}$–Ni, 1H), 3.13 (m, η^3-$\mathrm{H_a}H_b\mathrm{CC(H_c)C}H_b\mathrm{H_a}$–Ni, 2H), 2.51 (m, η^3-$H_a\mathrm{H_bCC(H_c)CH_b}H_a$–Ni, 2H). Anal. Calcd for $Ni_2C_{22}H_{18}N_2O_4$: C, 53.95%; H, 3.71%; N, 5.72%. Found: C, 53.79%; H, 3.30%; N, 5.54%.

Polymerizations of IV with Allyl–Nickel Catalysts under O_2. In the glovebox, **IIIc** (0.5 mg, 1.0 μmol), for example, dissolved in toluene (0.25 mL) was added to a 5-mL round-bottom flask which was capped with a septum. IV (100 mg, 0.76 mmol) was then added, and the resulting deep red solution was removed from the glovebox, put under an O_2 atmosphere by purging the flask with a needle, and stirred for 32 h. The resulting solid gel was thinned with toluene (3 mL) and then added to dilute KOH (0.01 M) in methanol to precipitate the polymer. The product was separated by centrifugation and then air dried. Reprecipitation and then drying *in vacuo* gave the polymer as an yellow/brown powder (94 mg, 94%). IR ($CHCl_3$): 1608 cm^{-1} (ν(CN), vs) (lit.[3] IR (Nujol): 1610 cm^{-1} (δ(CN), vs)).

Kinetic Measurements. Kinetic data were obtained by periodically removing aliquots from a thermostated polymerization, diluting these (100-fold) with chloroform to a known volume (1.0 mL), and recording the intensity of the isocyanide CN stretch of unreacted monomer by IR spectroscopy. Typical polymerization conditions were, for example, **IIId** (0.50 mg, 1.1 μmol) dissolved in toluene (0.250 mL) with *R*/*S*-**II** (0.10 mL, 0.73 mmol) under O_2 atmosphere. Isocyanide concentrations were determined by use of an empirical calibration curve (transmittance vs concentration) of **II** in chloroform. Monomer concentrations as functions of time were then fit to straight line plots using standard rate law equations.

***trans*-$(C_6H_5)Ni(PMe_3)_2Br$.**[39] In the drybox, to a 10-mL round-bottom flask containing a stirbar and Ni(1,5-cyclooctadiene)$_2$ (50.0 mg, 0.182 mmol) in ethyl ether (8 mL) were added trimethylphosphine (38.0 μL, 0.364 mmol) and bromobenzene (19.0 mL, 0.182 mmol). The reaction was let stir for 24 h whereupon the orange solution was filtered to remove a black precipitate. This solution was concentrated *in vacuo* and then cooled to –40 °C to produce the product as orange needles. The crystals were washed with cold (–40 °C) hexanes and then dried to leave the product (53 mg, 80%). ^{1}H NMR (C_6D_6): δ 7.32 (br d, Ar*H*, 2H), 6.95 (br t, Ar*H*, 2H), 6.80 (t, Ar*H*, 1H), 0.85 (t, P*Me*$_3$, 18H) (lit. ^{1}H NMR (CD_2Cl_2): δ 7.4–6.6 (m, Ar*H*, 4H), 0.87 (t, P*Me*$_3$, 18 H)). ^{31}P {^{1}H} NMR (C_6D_6): δ –9.32 (s, *trans*-*P*Me$_3$).

***trans*-$C_6H_5(Me_3CN)CNi(PMe_3)_2Br$.** In the drybox, to a 10-mL round-bottom flask containing a stirbar and *trans*-$(C_6H_5)Ni(PMe_3)_2Br$ (100 mg, 0.272 mmol) in ethyl ether (4 mL) was added *tert*-butyl isocyanide (30.5 μL, 0.272 mmol). The reaction was let stir for 1 h whereupon the solution was concentrated and then cooled to –40 °C to produce the product as orange prisms. The crystals were washed with cold (–40 °C) hexanes and then dried to leave the product (122 mg, 99.5%). IR (THF): 1568 cm^{-1} (ν(CN), m). ^{1}H NMR (C_6D_6): δ 8.90 (br d, Ar*H*, 2H), 2.71 (br t, Ar*H*, 2H), 7.11 (t, Ar*H*, 1H), 1.84 (s, C*Me*$_3$, 9H), 1.00 (t, P*Me*$_3$, 18H). ^{31}P {^{1}H} NMR (C_6D_6): δ –12.99 (s, *trans*-*P*Me$_3$). Anal. Calcd for $NiC_{17}H_{32}NP_2Br$: C, 45.27%; H, 7.17%; N, 3.10%. Found: C, 45.04%; H, 7.02%; N, 3.09%.

Reaction of PPh_3 with *trans*-$C_6H_5(Me_3CN)CNi(PMe_3)_2Br$. To an NMR tube containing *trans*-$C_6H_5(Me_3CN)CNi(PMe_3)_2Br$ (6.0 mg, 0.013 mmol) in C_6D_6 (0.5 mL) was added triphenylphosphine (10.0 mg, 0.040 mmol). The orange solution was heated in an oil bath at 50 °C for 5 days, during which the sample was removed daily and NMR spectra were taken. The resonances for *trans*-$C_6H_5(Me_3CN)CNi(PMe_3)_2Br$ were observed to decrease in intensity while resonances assigned to *N*-benzylidene-*tert*-butylamine (IR (C_6D_6): 2390 (ν(NC–H), w), 1639 cm^{-1} (ν(CN), m). ^{1}H NMR (C_6D_6): δ 8.12 (s, N═C*H*, 1H), 7.80 (br d, Ar*H*, 2H), 7.13 (m, Ar*H*, 3H), 1.23 (s, C*Me*$_3$, 9H).) and bis(*tert*-butyl)iminobenzil (IR(C_6D_6): 1617 cm^{-1} (ν(CN), m). ^{1}H NMR (C_6D_6): δ 7.73 (m, Ar*H*, 4H), 7.03 (m, Ar*H*, 6H), 0.87 (s, C*Me*$_3$, 9H), 0.85 (s, C*Me*$_3$, 9H).) grew in intensity. The reaction had gone to completion (no starting complexes observable) in *ca.* 4 days.

$[N(Bu)_4^+][(\eta^3\text{-}C_3H_5)Ni(CN)_2O_2CCF_3]^-$ (I(CN)Bu). In the glovebox, I (5.0 mg, 12.0 μmol) dissolved in toluene (5 mL) was added to a 10-mL round-bottom flask which was capped with a septum. $N(Bu)_4CN$ (6.3 mg, 24 μmol) dissolved in toluene (1 mL) was then added, causing the red solution to instantly turn pale yellow. Removal of the solvent *in vacuo* left the product as an orange oil (12 mg, 98%). IR (THF): 2143 (ν(CN), vs), 1693 cm^{-1} (ν(CO), vs). ^{1}H NMR ($CDCl_3$): 5.15 (br m, η^3-$\mathrm{H_aH_bCC}(H_c)\mathrm{CH_bH_a}$–Ni, 1H), 3.71 (m, η^3-$\mathrm{H_a}H_b\mathrm{CC(H_c)C}H_b\mathrm{H_a}$–Ni, 2H), 3.10 (br m, $\mathrm{N(C}H_2\mathrm{CH_2CH_2CH_3)_4^+}$, 8H), 2.23 (m, η^3-$H_a\mathrm{H_bCC(H_c)CH_b}H_a$–Ni, 2H), 1.57 (br m, $\mathrm{N(CH_2C}H_2\mathrm{CH_2CH_3)_4^+}$, 8H), 1.43 (br m, $\mathrm{N(CH_2CH_2C}H_2\mathrm{CH_3)_4^+}$, 8H), 1.00 (br t, $\mathrm{N(CH_2CH_2CH_2C}H_3\mathrm{)_4^+}$, 12H). ^{19}F NMR ($CDCl_3$): δ –72.57 (s, CF_3).

$2[N(Bu)_4^+][(\eta^3\text{-}C_3H_5)Ni(CN)_2O_2CCF_3]^{2-}$ (I(CN)$_2$-Bu). In the glovebox, I (5.0 mg, 12.0 μmol) dissolved in toluene (5 mL) was added to a 10-mL round-bottom flask which was capped with a septum. $N(Bu)_4CN$ (12.6 mg, 48 μmol) dissolved in toluene (1 mL) was then added, causing the red solution to instantly turn pale yellow. Removal of the solvent *in vacuo* left the product as an orange oil (17.5 mg, 99%). IR (THF): 2110, 2082 (1:1, ν(CN), vs), 1691 cm^{-1} (ν(CO), vs). ^{1}H NMR ($CDCl_3$): 4.85 (br m, η^3-$\mathrm{H_aH_bCC}(H_c)\mathrm{CH_bH_a}$–Ni, 1H), 3.66 (m, η^3-$\mathrm{H_a}H_b\mathrm{CC(H_c)C}H_b\mathrm{H_a}$–Ni, 2H), 3.31 (br m, $\mathrm{N(C}H_2\mathrm{CH_2CH_2CH_3)_4^+}$, 16H), 2.22 (br d, η^3-$H_a\mathrm{H_bCC(H_c)CH_b}H_a$–Ni, 2H), 1.66 (br m, $\mathrm{N(CH_2C}H_2\mathrm{CH_2CH_3)_4^+}$, 16H), 1.44 (br m, $\mathrm{N(CH_2CH_2C}H_2\mathrm{CH_3)_4^+}$, 16H), 1.00 (br t, $\mathrm{N(CH_2CH_2CH_2C}H_3\mathrm{)_4^+}$, 24H). ^{19}F NMR ($CDCl_3$): δ –72.45 (s, CF_3).

$3[N(Bu)_4^+][(\eta^3\text{-}C_3H_5)Ni(CN)_2O_2CCF_3]^{3-}$ (I(CN)$_3$Bu). In the glovebox, I (5.0 mg, 12.0 μmol) dissolved in toluene (5 mL) was added to a 10-mL round-bottom flask which was capped with a septum. $N(Bu)_4CN$ (18.9 mg, 72 μmol) dissolved in toluene (1 mL) was then added, causing the red solution to instantly turn pale yellow. Removal of the solvent *in vacuo* left the product as an orange oil (23.5 mg, 98%). IR (THF): 2110, 2082 (1:2, ν(CN), vs), 1690 cm^{-1} (ν(CO), vs). ^{1}H NMR ($CDCl_3$): unobserved (η^1-$\mathrm{H_aH_bCC}(H_c)\mathrm{CH_bH_a}$–Ni, 1H), 4.85 (m, η^1-$\mathrm{H_a}H_b\mathrm{CC(H_c)C}H_b\mathrm{H_a}$–Ni, 2H), 3.33 (br m, $\mathrm{N(C}H_2\mathrm{CH_2CH_2CH_3)_4^+}$, 24H), unobserved ($\eta^1$-$H_a\mathrm{H_bCC(H_c)CH_b}H_a$–Ni, 2H), 1.66 (br m, $\mathrm{N(CH_2C}H_2\mathrm{CH_2CH_3)_4^+}$, 24H), 1.44 (br m, $\mathrm{N(CH_2CH_2C}H_2\mathrm{CH_3)_4^+}$, 24H), 0.98 (br t, $\mathrm{N(CH_2CH_2CH_2C}H_3\mathrm{)_4^+}$, 36H). ^{19}F NMR ($CDCl_3$): δ –72.47 (s, CF_3).

Polymerization of $CH_3(CH_2)_5NC$ with I under O_2. In the glovebox, I (0.5 mg, 1.2 μmol) dissolved in toluene (0.25 mL) was added to a 5-mL round-bottom flask which was capped with a septum. $CH_3(CH_2)_5NC$ (77 mg, 0.69 mmol) was then added, and the resulting dark brown solution was removed from the glovebox, put under an O_2 atmosphere, and stirred for 16 h. The resulting solid black gel was thinned with toluene (3 mL) and then added to dilute KOH (0.01 M) in methanol to precipitate the polymer. The product was separated out by centrifugation and then air dried. Reprecipitation and then drying *in vacuo* gave the polymer as an black/brown powder (49 mg, 98%). IR ($CHCl_3$): 1608 cm^{-1} (ν(CN), vs) (lit[33] IR (Nujol): 1620 cm^{-1} (ν(CN), vs)). GPC analysis: $\bar{M}_n$ = 2180, $\bar{M}_w$ = 4610, PDI = 2.1.

Polymerization of $CH_3(CH_2)_5NC$ with I(CN)$_2$Bu under O_2. In the glovebox, I(CN)$_2$Bu (0.7 mg, 0.94 μmol) dissolved in acetonitrile (0.20 mL) was added to a 5-mL round-bottom flask which was capped with a septum. $CH_3(CH_2)_5NC$ (30.1 mg, 0.28 mmol) was then added, and the resulting yellow solution was removed from the glovebox, put under an O_2 atmosphere, and stirred for 16 h. The resulting solid orange gel was thinned with toluene (3 mL) and then added to dilute KOH (0.01 M) in methanol to precipitate the polymer. The product was separated out by centrifugation and then air dried. Reprecipitation and then drying *in vacuo* gave the polymer as a sticky light tan powder (19 mg, 63%). IR ($CHCl_3$): 1622 cm^{-1} ($\nu(\underline{C}N)$, vs) (lit[33] IR (Nujol): 1620 cm^{-1} (ν(CN), vs)). GPC analysis: $\overline{M}_n$ = 16 710, PDI = 2.1.

Polymerization of $CH_3(CH_2)_5NC$ with $I(CN)_2Bu$ under O_2. In the glovebox, $I(CN)_2Bu$ (0.7 mg, 0.94 μmol) dissolved in acetonitrile (0.20 mL) was added to a 5-mL round-bottom flask which was capped with a septum. $CH_3(CH_2)_5NC$ (60.2 mg, 0.56 mmol) was then added, and the resulting yellow solution was removed from the glovebox, put under an O_2 atmosphere, and stirred for 16 h. The resulting solid orange gel was thinned with toluene (3 mL) and then added to dilute KOH (0.01 M) in methanol to precipitate the polymer. The product was separated out by centrifugation and then air dried. Reprecipitation and then drying *in vacuo* gave the polymer as a sticky light tan powder (52 mg, 86%). IR ($CHCl_3$): 1622 cm^{-1} ($\nu(\underline{C}N)$, vs) (lit[33] IR (Nujol): 1620 cm^{-1} (ν(CN), vs)). GPC analysis: $\overline{M}_n$ = 36 270, PDI = 2.5.

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