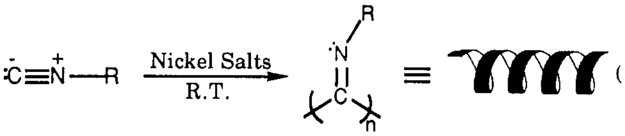
Communications to the Editor

Organometallic Catalysis in Air and Water: Oxygen-Enhanced, Nickel-Catalyzed Polymerizations of Isocyanides

For toxicological, environmental, processing, and kinetic reasons, it is considered highly desirable to carry out industrial polymerizations in aqueous solution.[1] Consequently, we have been interested in developing methods for the promotion of normally sensitive transition-metal-catalyzed polymerizations from the realm of rigorously dry organic solvents to 100% aqueous solution. This goal requires the development of unique carbon–carbon bond formation reactions mediated by transition metals in an aqueous environment. Recent successes with aqueous ring-opening metathesis polymerizations[2] have led to the encouraging conclusion that, with the proper choice of catalyst, many transition-metal-catalyzed polymerizations can be carried out in aqueous media.[3]

For independent reasons, we have been interested in developing catalysts for the controlled polymerization of isocyanides to form liquid-crystalline polymers possessing stable, rodlike helical conformations (eq 1).[4] Interest in these unique materials has recently intensified following the discovery that, with bulky substituents, these helices can be isolated in optically active form.[5] The polymerization of bulky isocyanides is, however, limited in that the size of the isonitrile's substituent is inversely related to the yield of polymer obtained.[4]



(1)

In our efforts to develop highly active nickel catalysts, which would allow control over the polymerization and hence the nature of polymer end product, we have found that carrying out nickel-catalyzed polymerizations in the presence of water and under an atmosphere of air actually decreases initiation periods, enhances polymerization rates, and increases the overall yields of polymer. Furthermore, excess water does not deactivate the catalyst, and indeed the polymerization proceeds in aqueous solutions with pH values ranging from 2 to 12. Thus, this polymerization represents a multiple carbon–carbon bond formation reaction that thrives under conditions normally considered destructive for organometallic catalysis.[6] Furthermore, mechanistic insights gained during this study have led to the design of highly active catalysts that *quantitatively polymerize* even the most truculent isocyanides.

Literature reports describe the quantitative polymerization of unhindered isocyanides by nickel(II) salts under nitrogen in anhydrous ethanol in a few (~5) hours.[4] The proposed mechanism[4] for this process assumes the formation of a square-planar, tetrakis(isocyanide)nickel(II) complex, which acts as a template upon which propagation occurs via multiple isocyanide migratory-insertion steps. Our initial work in this area indicated that nickel-catalyzed polymerizations were far more complex than depicted in this mechanism and that the reaction can actually be cocatalyzed by oxidizing agents such as oxygen.

Our attempts to reproduce literature polymerization results under nitrogen in either tetrahydrofuran (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 gave high yields (>90%) of polymer in less than 1 h. Passing oxygen over a sluggish polymerization run under nitrogen led to an immediate increase in polymer formation.[8] Other oxidizing agents, e.g., $K_2S_2O_8$, gave similar increases in rate and yield of polymer.[9] Yet, the addition of oxygen at best represents a compromise. When oxygen was bubbled continuously through a polymerization mixture, the polymer yield decreased dramatically.[10] Similarly, a solution of *tert*-butyl isocyanide (0.88 M) and *trans*-$NiCl_2[CNC(CH_3)_3]_2$ (0.020 M) in THF gave, after purging with oxygen for 1 h, nearly quantitative conversion to the corresponding *tert*-butyl isocyanate.[11] To account for the behavior of oxygen, we initially believed that oxygen might be oxidizing nickel(II) to a nickel(III) species, which could then be the active polymerization catalyst. The fact that isocyanides can act as potent reducing agents,[12] however, forced us to consider a mechanism wherein nickel(II) is reduced to an inactive or highly inactive nickel(I) catalyst by isocyanide and then reoxidized to a more catalytically active nickel(II) species by oxygen. Experimental investigations support this latter mechanism.

Direct evidence for the reduction of nickel(II) to nickel(I) by isocyanides under typical polymerization conditions was obtained by using ESR, cyclic voltammetry, and bulk magnetic susceptibility measurements. ESR spectra[13] of frozen catalyst solutions[14] were recorded at 77 K with and without isocyanide and/or oxygen purging. Both nickel(I) and nickel(III) exhibit characteristic ESR signals[15] while no signal is usually observed for paramagnetic nickel(II) under these conditions.[15,16] 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 nitrogen, 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.[15] When the solutions were purged with oxygen, the ESR signals disappeared and the catalyst was presumably converted back to nickel(II), consistent with oxygen acting as an oxidizing agent. These ESR data suggest that, under polymerization conditions, the active nickel catalyst has been reduced to a nickel(I) species and has a trigonal-bipyramidal structure,[15] which conflicts with the nickel(II) isocyanide complexes[17] that have been proposed as active catalytic species for isocyanide polymerizations under nitrogen.[4]

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.[18] In all solvents studied,[19] the catalysts clearly underwent transformation from nickel(II) complexes ($\mu_{eff} = 2.99\ \mu_B$),[20] to predominantly nickel(I) complexes ($\mu_{eff} = 2.25\ \mu_B$)[20] upon the addition of 10 equiv of *tert*-butyl isocyanide, and the back to the nickel(II) state ($\mu_{eff} = 2.94\ \mu_B$) upon purging with dioxygen. Because susceptibility

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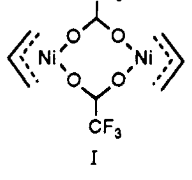
is a bulk property, these results can be qualitatively interpreted to indicate that the *bulk* of the nickel catalyst (as opposed to merely a minute fraction) is converted to the nickel(I) state by isocyanide and then back to the nickel(II) state by oxygen. Further evidence for the nickel(I) oxidation state was obtained by an experiment wherein a different reducing agent, hydrazine, was added and similar behavior observed.[21]

To further quantify these redox properties, cyclic voltammograms of catalyst solutions in water were recorded.[22] We found that addition of 10 equiv of isocyanide to $NiCl_2$ solutions (under nitrogen) showed a reversible, one-electron wave with $E_{1/2} = -0.341$ V vs SCE for the Ni(I)/Ni(II) couple.[23] 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 oxygen resulted in 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 ($\geq$10 equiv) isocyanide since well-characterized nickel(II) isocyanide complexes can be isolated.[24]

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,[25] the nickel(I) complex appears itself to be a mild catalyst. Far more active catalysts can be realized by the controlled introduction of oxidizing agents (i.e., oxygen). Although more detailed studies are underway, it appears that the optimum dioxygen concentration for polymerization may be that found serendipitously, i.e., 1 atm of air. In summary, we have found the isocyanide/nickel catalytic system apparently encompasses a triple catalytic cycle in which isocyanides can be polymerized very slowly by a nickel(I) species or rapidly by a nickel(II) species or can be oxidized to their corresponding isocyanates.

Our observation that Ni(II) complexes are rapidly reduced to Ni(I) (and hence, deactivated), in the presence of excess isocyanide, spurred us to consider incorporating strongly electron-withdrawing groups on the catalyst center in order to activate coordinated isocyanides toward nucleophilic attack. In addition, as the initiation step is also thought to involve attack on a bound isocyanide,[4] we thought it advantageous to incorporate an intramolecular nucleophile that could undergo a migratory-insertion reaction with a coordinated isocyanide and thereby facilitate the initiation process. Accordingly, we synthesized η^3-allylnickel trifluoroacetate, I,[26] a single-component catalyst that combines both of the following features: an allyl group, which is known to undergo migratory-insertion reactions with isocyanides, and an activating trifluoroacetate to remove electron density from the nickel center.



I

Table I
Molecular Weight Characteristics of Selected Polymers[28]

monomer	catalyst	conditions	yield, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
tert-C_4H_9NC	I	N_2, neat	100	2 200	1.03
$C_6H_5CH(CH_3)NC$	$NiCl_2$	N_2, H_2O	75	13 220	1.45
$C_6H_5CH(CH_3)NC$	$NiCl_2$	air, H_2O	100	7 420	1.64
$C_6H_5CH(CH_3)NC$	I	N_2, toluene	100	24 000	1.15

Consistent with the above discussion, we have found that I polymerizes cyclohexyl isocyanide in quantitative yield in a matter of seconds at room temperature. This compares favorably with literature yields of 10% in nonpolar solvent after 5 h at 75 °C using $NiCl_2$. Likewise, bulky, unreactive *tert*-butyl isocyanide is *quantitatively* polymerized by I in a matter of hours. To our knowledge, the best literature comparison is a heterogeneous system that produced a 37% yield of poly(*tert*-butyl isocyanide) after 3 days.[4] Molecular weight characteristics of our poly(*tert*-butyl isocyanide) as well as soluble poly(α-methylbenzyl isocyanide)[27] samples, prepared under a variety of conditions, are listed in Table I. The admission of oxygen to polymerizations using I gave substantial increases in the already fast polymerization rates, consistent with our observations described earlier.

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(7) For example, 0.01 M $NiCl_2$ in ethanol with 2.0 M cyclohexyl isocyanide monomer under dinitrogen gave a 50% yield of polymer after 20 h.

(8) For example, 0.01 M $NiCl_2$ in ethanol with 2.0 M cyclohexyl isocyanide monomer under 1 atm of air gave a 95% yield of polymer in 3 h.

(9) Polymerization was run under dinitrogen as in ref 7 but with 50 equiv of $K_2S_2O_8$ added. The polymer yield after 5 h was 98%. $K_2S_2O_8$ by itself was not observed to polymerize isocyanides.

(10) For example, 0.01 M $NiCl_2$ with 2.0 M cyclohexyl isocyanide in water gave a polymer yield of 6.3% after 20 h.

(11) $(CH_3)_3CNC$: ν_{CN} = 2135 cm^{-1}; ^{1}H NMR (THF-d_8) δ 1.55 (t, $(CH_3)_3CNC$, 9 H). $(CH_3)_3NCO$: ν_{CNO} = 2259 cm^{-1}; ^{1}H NMR (THF-d_8) δ 1.68 (s, $(CH_3)_3CNCO$, 9 H). IR spectra were recorded by using THF solutions pressed between NaCl disks on a Nicolet 5DX FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer and referenced by assigning the β-methylene residual protons in THF-d_8 to 1.78

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(13) ESR spectra were recorded by using a Bruker ER 200D-SRC X-band spectrometer, and *g*-values were referenced to external DPPH at $g = 2.0037$.

(14) ESR solutions consisted of $NiCl_2$ in ethanol and $NiCl_2((CH_3)_3CNC)_2$ in THF and toluene. All solvents were anhydrous. Generally, 10 equiv of *tert*-butyl isocyanide was added to the solutions immediately before recording the spectra.

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(18) The Evans[29] method was used on either a Bruker AM-400 or AM-500 NMR spectrometer. THF and toluene were dried by distillation from Na/benzophenone, methanol and water were purged with dinitrogen for 20 min before use.

(19) $NiCl_2$ with 10 equiv of *tert*-butyl isocyanide in water and methanol and $NiCl_2((CH_3)_3CNC)_2$ with 10 equiv of *tert*-butyl isocyanide in THF and toluene were used.

(20) μ_{eff}(nickel(II)) = 2.9–3.4 μ_B; μ_{eff}(nickel(I)) = 1.9–2.3 μ_B from ref 12.

(21) $\mu_{eff} = 2.46\ \mu_B$. Hydrazine added to a polymerization also lowered the yield of polymer to 25%.

(22) Conditions: 0.01 M $NiCl_2$, 20 equiv of *tert*-butyl isocyanide, 0.1 M NaCl in water with Pt wire as the working electrode, Ag wire as a pseudo reference electrode, and glassy carbon as the counter electrode. Scan rate = 50 mV/s. Potassium ferrocyanide was used as an internal reference, and potentials were then referenced back to SCE.

(23) Literature values for Ni(I)/Ni(II) couples (mostly for macrocyclic ligand complexes) range from $E_{1/2} = -1.2$ V to $E_{1/2} = -0.3$ V vs SCE.[30]

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(25) $NiCl_2$ solution in water and isocyanide were freeze-pump-thaw degassed on a vacuum line and then mixed without exposure to any external atmosphere.

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(27) Poly(α-methylbenzyl isocyanide) samples were prepared in a manner analogous to the preparation of poly(cyclohexyl isocyanide).[7,8]

(28) Molecular weights were determined by using gel permeation chromatography (GPC), which was done with 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-, and 10^3-Å Waters Ultrastyragel columns, and the molecular weight was calibrated relative to polystyrene standards.

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Registry No. I, 32823-77-1; $NiCl_2$, 7718-54-9; $t\text{-}C_4H_9NC$ (homopolymer), 28513-62-4; $C_6H_5CH(CH_3)NC$ (homopolymer), 29499-57-8.