Macromolecules **1991,** *24,* 6043–6045

Communications to the Editor

Polyisocyanides Using $[(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)]_2$: Rational Design and Implementation of a Living Polymerization Catalyst

Since their discovery over 20 years ago, polyisocyanides[1] have been the focus of intense research efforts due to the unusual stability of the helical conformation adopted by select members of this family.[2] During our investigations into the development of active, homogeneous catalysts for the polymerization of isocyanides, we have discovered the catalyst $[(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)]_2$ (I) to be very effective in this regard.[3] We herein report the first "living" polymerization of isocyanides using homogeneous complex I, which provides quantitative yields of polyisocyanides and diblock copolymers possessing controlled molecular weight and narrow polydispersities.

Polyisocyanides were first prepared by Millich who used a heterogeneous ground glass–sulfuric acid–O_2 catalyst system.[1] The discovery by Drenth and co-workers[4] that simple nickel salts (e.g., $NiCl_2$, $Ni(acac)_2$, etc.) catalyzed the polymerization of isocyanides was a substantial improvement; however, these polymerizations were not living, provided little control over molecular weight, and gave polymers with broad polydispersities (typically ranging from 2 to 6).[5] Furthermore, the reactions are heterogeneous as they require polar, protic solvents such as ethanol, which are nonsolvents for the polyisocyanides. This heterogeneity is a severe encumbrance to the design of a living system. Homogeneous polymerizations in toluene, a good polymer solvent, either were exceedingly inefficient (i.e., 10% yield after 5 h at 75 °C)[4a] or failed altogether.

During our initial studies of the nickel-catalyzed systems, we discovered that, under polymerization conditions, the isocyanide monomer acts as a potent reducing agent for nickel(II) to give nickel(I) complexes and that oxygen acts to cocatalyze the reaction.[3] Furthermore, we found a pronounced increase in the rate of initiation upon the addition of nucleophiles (e.g., CH_3Li) to the reaction.[6] In combination, these two facts led us to investigate η^3-allylnickel trifluoroacetate, I,[7] possessing the electron-withdrawing trifluoroacetate ligand to remove electron density from the reduced nickel center and the allyl group which is known to undergo migratory-insertion reactions with isocyanides.[8] We have shown that I rapidly and homogeneously polymerizes sterically unhindered isocyanides (α-methylbenzyl isocyanide, II (racemic and/or the pure enantiomers)), in aprotic solvents and is also able to polymerize bulky isocyanides (i.e., *tert*-butyl isocyanide, III) in quantitative yields.[3]

Although homogeneous and mildly active ($k_{obs} = 8.1 \times 10^{-6}\ s^{-1}$), catalyst I was found to display classic, nonliving, chain-growth behavior for the polymerization of II in THF solution, as evidenced by the formation of high molecular weight chains at very low monomer conversion (i.e., $\bar{M}_n$ - 57 000 at 5% conversion). Switching to a noncoordinating solvent (toluene), however, led to a near 10-fold increase in catalyst activity and living behavior in the system.

Living polymerizations are polymerizations which proceed without chain-transfer or chain-termination steps.[9] In the absence of chain-transfer steps, a linear increase in the average molecular weight as a function of monomer conversion should be realized.[10] Indeed, this linear behavior was observed in the polymerization of II with I under a variety of conditions (Figure 1). $\bar{M}_n$ was determined by GPC, and percent conversion was determined by correlating reaction time with kinetic data (vide infra). Furthermore, the average molecular weights of the isolated polymers varied linearly with the monomer to catalyst ratio (Table I), which is also characteristic of a living system. The molecular weight distributions of these polymers ranged on average from $\bar{M}_w/\bar{M}_n$ = 1.1 to 1.6.

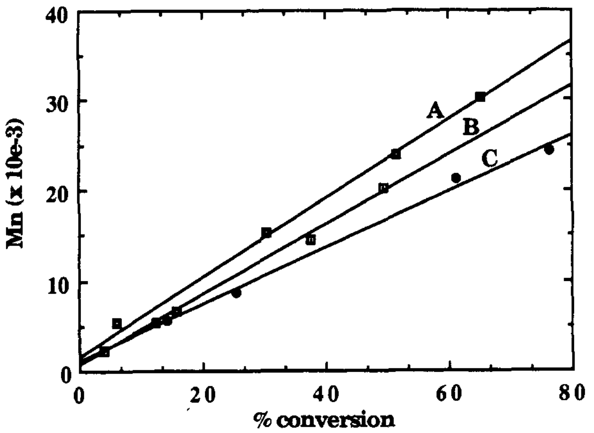

Figure 1. Graphs of molecular weight ($\bar{M}_n$) vs percent conversion of monomer for different reaction conditions: (A) in toluene–H_2O under N_2; (B) in toluene under N_2; (C) in toluene under O_2.

Table I
Variation of Molecular Weight with Monomer/Catalyst Feed Ratio

mol of II/mol of Ni	39	78	156	779
$\bar{M}_n$(GPC)[a]	3240	8580	24100	82700

[a] Molecular weights are relative to polystyrene standards.

Chain-termination steps can be detected by monitoring the rate of polymerization as a function of time.[10] Linearity in this kinetic analysis was consistent with a fixed number of active sites throughout the lifetime of the reaction. We have measured the kinetic behavior of II using complex I under both N_2 and O_2 and found linear behavior well past 3 half-lives in both cases, which indicated the absence of chain-termination processes. Under N_2, the polymerization was found to be first order in monomer with k_{obs}(298 K) = 4.4 (1) × $10^{-5}\ s^{-1}$, and under O_2 the rate was found to be zero order in monomer with k_{obs}(298 K) = 6.3 (1) × $10^{-5}\ mol{\cdot}L^{-1}{\cdot}s^{-1}$. The previously reported[3] redox behavior [Ni(I)/Ni(II)] of the catalyst probably caused the differences in observed order, which consequently gave rise to the substantial overall rate enhancement of the polymerization under O_2 (i.e., given comparable rate constants, a zero-order reaction will always be faster than a first-order reaction). Given the significant changes in both the nature of the catalyst and the rate-determining step in going from an atmosphere of N_2 to O_2, we found it quite surprising and interesting that the polymerization of II remains living under an O_2 atmosphere. As shown in

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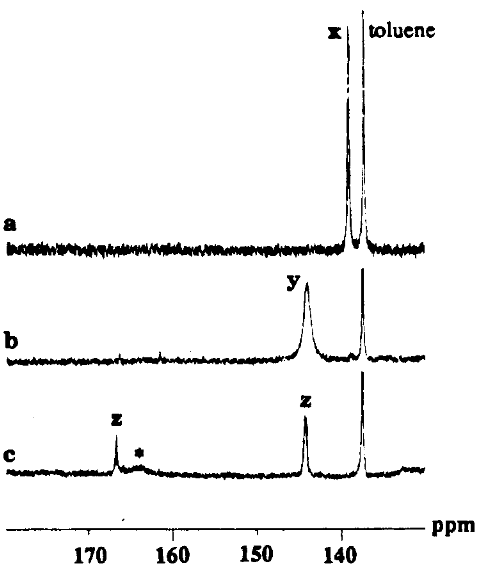

Figure 2. Partial $^{13}C\{^1H\}$ NMR spectra taken after the sequential addition of one, two, and three (a–c, respectively) equivalents per nickel center of 98% ^{13}C-enriched II to I in toluene-d_8 at −60 °C. Assignments: (x) (η^3-C_3H_5)Ni(OC(O)CF_3)^{13}CNR; (y) (η^1-C_3H_5)Ni(OC(O)CF_3)(^{13}CNR)$_2$; (z) [$CH_2CHCH_2{}^{13}C$(NR)]-Ni(OC(O)CF_3)(^{13}CNR)$_2$; (*) polymer.

Table II
Sample GPC Data for Block Copolymers

segment 1	segment 2	$\bar{M}_n$ (segment 1)	$\bar{M}_n$ (copolymer)
poly(II)	poly(II)	73 960	96 670
poly(II)	poly(*t*-BuNC)	31 040	34 210

Figure 1, the presence of water had little effect on the polymerization, further illustrating the robust nature of the catalyst.

Presumably, initiation of the polymerization proceeds through insertion of an isocyanide into the allyl–nickel bond of I to afford an iminoacyl–nickel complex, which could then act as the propagating species in the polymerization process.[4] In an effort to investigate this initiation mechanism, we synthesized II 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 2 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 2a).[11] Addition of a second equivalent of monomer presumably resulted in the formation of a η^1-allyl-bis(isocyanide) complex (Figure 2b). Addition of a third equivalent of isocyanide gave a spectrum assignable to the insertion product (Figure 2c),[12] 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.

The living nature of these polymerizations as well as the synthetic utility of I was demonstrated by the successful preparation of isocyanide–isocyanide block copolymers.[13] These block copolymers were prepared by the polymerization of II by I followed by addition of either II or *tert*-butyl isocyanide, III, to afford the copolymers which were characterized by both GPC (Table II) and NMR. Since the conformational structures of polyisocyanides are highly dependent upon the steric bulk of the isocyanide substituent,[2] these block copolymers illustrate the ability to covalently bond liquid-crystalline, rodlike, helical segments (poly(*tert*-butyl isocyanide)) to more flexible segments (poly(II)).[2]

The number of transition-metal-catalyzed polyermizations which display all of the characterstics of living systems is limited.[14] We feel, however, that the versatility inherent in organometallic complexes (i.e., variable oxidation states, Lewis acidities, ligand spheres, etc.) offers the potential for authoritatively controlling the activity and selectivity of the propagating end group. Hence, these complexes may provide the foundation upon which other living polymerization systems can be developed.

Acknowledgment. This work was supported by University of California "Start-up Funds", the National Science Foundation (Grant No. CHE-9023253) and generous contributions from E.I. du Pont de Nemours and Co., the Exxon Corp., and Chevron Research. T.J.D. gratefully acknowledges the NSF for a graduate fellowship.

Supplementary Material Available: Experimental procedures for all of the polymerizations and spectral and characterizational techniques (3 pages). Ordering information is given on any current masthead page.

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(15) Alfred P. Sloan Fellow, 1991–92; Presidential Young Investigator, 1991–96.

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Received June 18, 1991
Revised Manuscript Received August 23, 1991

Registry No. I, 32823-77-1; II (homopolymer), 29499-57-8; II–III (block copolymer), 136391-38-3; II–III (copolymer), 136391-39-4; II, 17329-20-3.