# Living Organotitanium(IV)-Catalyzed Polymerizations of Isocyanates

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**Abstract:** An organotitanium(IV) compound, $TiCl_3OCH_2CF_3$, **1**, was found to polymerize *n*-hexyl isocyanate to high yields and without the formation of cyclic trimer. $CpTiCl_2L$ (L = $-OCH_2CF_3$, $-N(CH_3)_2$, $-CH_3$), **2**−**4**, respectively, likewise polymerized *n*-hexyl isocyanate but also polymerized isocyanates in the presence of donor solvents and isocyanates possessing donor functional groups, activated olefins, and strained olefins. The activity of the organotitanium(IV) catalysts decreased with increasing steric bulk about the metal center and increasing electron donation to the metal center from the ligands. The polymerization of *n*-hexyl isocyanate using organotitanium(IV) compounds is living. The PDIs of PHIC synthesized using catalysts **1**−**4** were found to range from 1.05 to 1.2. The molecular weight of the polymer formed in polymerizations of *n*-hexyl isocyanate using catalysts **1**−**4** varied linearly as a function of the monomer-to-initiator ratio and the percent conversion of the polymerization. Polymerizations using **2** can be endcapped quantitatively, and well-defined block copolymers can be synthesized using catalysts **1**−**4**. The kinetics for polymerizations using catalysts **1** and **2** are first-order in both monomer and catalyst ($k_1 = 8.5 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$, $k_{-1} = 3.8 \times 10^{-4}$ $s^{-1}$). The active endgroup of a polymerization using **3** was observed using IR spectroscopy, and the frequency of the IR stretch (1548 $cm^{-1}$) was consistent with an $\eta^2$-amidate endgroup structure. Finally, the kinetic data for the polymerization of *n*-hexyl isocyanate and the known chemistry of $CpTiCl_2L$ compounds were found to be consistent with a propagation step that occurs via a bifunctional activation mechanism.

## Introduction

One of the most important classes of polymerizations is the living polymerization,[3] which is a chain growth polymerization that proceeds in the absence of the kinetics steps of chain termination and chain transfer. In other words, during the time scale of the polymerization the only reaction pathway available to the active chain end is propagation. Living polymerizations are highly valued, because the molecular weight of the polymer formed can be established simply by varying the monomer-to-initiator ratio and because the molecular weight distribution of the resulting sample is very narrow. These types of polymerizations also permit the synthesis of well-defined block copolymers, since after completion of the polymerization the active chain ends persist until terminated or until an amount of the same or another monomer is added to the polymerization medium.[4]

Polyisocyanates are an unusual class of macromolecules, because they are one of the few types of synthetic polymers that adopt a stable helical conformation in solution as well as the solid state. Fiber diffraction experiments demonstrated that poly(*n*-butyl isocyanate) [PBIC] adopts an 8/3 helical conformation in the solid state.[5] Static characterization methods, such as light-scattering,[6] osmotic pressure[7] and electric dichroism measurements,[8] and dynamic characterization methods, such as dielectric,[9] mechanically- or electrically-induced birefringence,[10] and viscometric measurements,[11] demonstrated that poly(alkyl isocyanates) are stiff-chain polymers whose hydrodynamic properties are highly temperature-, solvent-, and molecular-weight-dependent. At lower molecular weights these polymers behave as true rigid rods, while at very high molecular weights they behave as semiflexible chains or “worm-like” polymers. The dynamic stereochemical properties of polyisocyanates have also been well-characterized. Because the helix is a chiral topological form and occurs with either a left-handed (M) or right-handed (P) screw sense, the backbone of polyisocyanates is inherently chiral, as observed in the X-ray fiber diffraction study of PBIC.[5] In several studies, remarkably large optical activities, associated with the polymer backbone chromophore, have been observed for polyisocyanate homo- and copolymers of optically active isocyanates.[12]

In 1960, Shashoua and co-workers reported the anionic polymerization of a variety of isocyanates using NaCN as the initiator and polar solvents, such as dimethylformamide (eq 1).[13]

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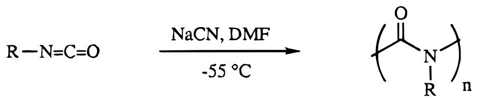
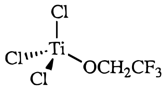


(1)

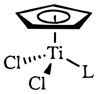
The authors examined polymerization temperatures ranging from −20 °C to −100 °C and found that the optimum temperature for polymerization to proceed in high yield was between −50 and −70 °C. Initiation of the anionic polymerization of isocyanates is proposed to occur by attack of the cyanide anion onto the electrophillic carbon of the isocyanate group to form an amidate anion. This anion acts as the propagating species and can add further isocyanate monomers or be terminated by added or adventitious protic sources.

The anionic polymerization of isocyanates is not living. Although no individual, comprehensive study of molecular weight control in anionic isocyanate polymerizations has been reported, experiments from several published reports can be assembled to demonstrate a lack of well-controlled, living behavior. Various authors have published results on the control of molecular weight as a function of the monomer-to-initiator ratio in anionic isocyanate polymerizations. Both Owadh et al.[14] and Shashoua et al.[13] observed that the molecular weight of anionically polymerized *n*-alkyl isocyanates showed little or no dependence upon the monomer-to-initiator ratio. By carefully performing *n*-butyl isocyanate polymerizations with high monomer-to-initiator ratios, Ahmed et al. did observe a relationship between the molecular weight ($M_v$) of the polymer and the monomer-to-initiator ratio.[15] However, the reported absolute molecular weights, on average, were greater than the expected molecular weights by an order of magnitude, and the observed relationship between $M_v$ and the monomer-to-initiator ratio was curved and not linear. Natta and co-workers observed that the inherent viscosity of anionic PBIC increased with increasing time and percent yield;[16] however, a plot of the authors' data as molecular weight ($M_v$) versus the percent yield of the polymerization reveals that the linear-like increase in molecular weight did not begin until the polymerization was at about 20% completion or greater. Moreover, the experimental molecular weights were too high by one-to-two orders of magnitude. The polydispersities [PDIs] of anionically polymerized *n*-butyl isocyanate and *n*-hexyl isocyanate were reported in only a few instances. Fetters and Yu measured $M_n$ (membrane osmometry) and $M_w$ (static light-scattering) values for a wide range of PHIC and PBIC samples prepared using alkyllithium and NaCN initiators and found that the PDIs varied from 1.1−9.5, with the average value being 3.7.[17] Okamoto et al., using a gel permeation chromatography [GPC] apparatus calibrated with their own fractionated poly(*n*-hexyl isocyanate) [PHIC] standards, found that the PDIs of their PHIC samples prepared using NaCN initiator varied from 1.2 to 1.8.[18] These results indicate that side reactions early in the polymerization, such as end-biting and spirotetramerization, significantly obstruct molecular weight control in the anionic polymerization of isocyanates. Furthermore, another side reaction, cyclic trimerization, can degrade the active polymer chains when polymerizations are conducted above a certain maximum temperature.

Some work has been done on alternative methods (cationic, free-radical, electrochemical, irradiative, and a few transition metal) of polymerizing isocyanates with little success.[19] Recently we communicated the use of organotitanium(IV) compounds as catalysts for the living polymerization of isocyanates.[20] In contrast to the anionic polymerization of isocyanates, these polymerizations exhibit excellent control over the molecular weight and polydispersity of the resulting polymer. We report here a complete account of the living polymerization of isocyanates using $TiCl_3OCH_2CF_3$, **1**, and $CpTiCl_2L$ ($L = -OCH_2CF_3$, $-N(CH_3)_2$, $-CH_3$), **2**−**4**, respectively, as catalysts including a complete assessment of the living behavior of the polymerizations along with kinetic and mechanistic investigations.



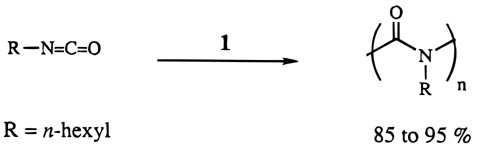
**1**



**2**: L = $-OCH_2CF_3$,
**3**: L = $-N(CH_3)_2$,
**4**: L = $-CH_3$

## Results and Discussion

**Overview of the Polymerizations.** When *n*-hexyl isocyanate is added to a concentrated solution of catalyst **1**, an orange solution is formed which then increases in viscosity until it eventually solidifies. A waxy, colorless solid is isolated upon workup, typically in 85−95% yields (eq 2). Cyclic trimer has not been isolated from or detected in these polymerizations. GPC, elemental analysis, $^1H$ NMR spectroscopy, and $^{13}C\{^1H\}$ NMR spectroscopy together confirm the formulation of this product as PHIC. In a series of polymerizations, a plot of the molecular weight of the polymer as a function of the monomer-to-initiator ratio can be fitted with a straight line with a slope near that of the molecular weight of the monomer repeat unit (Figure 1). When polymer samples are taken from a polymerization at various times, a plot of the samples' molecular weights as a function of percent conversion can be fitted with a straight line.[20] The polydispersities of these polymerizations typically fall within the range of 1.1−1.2. The bis-THF complex of **1**, $TiCl_3(OCH_2CF_3)(THF)_2$, behaves identically as **1** in isocyanate polymerizations.



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These polymerizations are necessarily conducted in either bulk or concentrated solutions due to the strong dependence of the yield of the polymerization upon the initial concentration of the monomer. When a polymerization of *n*-hexyl isocyanate was monitored using IR spectroscopy, the monomer concentration decreased throughout the course of the polymerization, but the concentration asymptotically approached a nonzero value (Figure 2). The aforementioned molecular weight control experiments preclude the possibility that this nonzero limit is indicative of termination processes. When more monomer was added to a polymerization in this state, propagation of the polymerization ensued until most of the added monomer was consumed. A comparison of GPC chromatograms of the polymer before and after this addition revealed that the additional monomer was incorporated into existing polymer chains and that no new polymer chains had formed. The GPC peak for the polymer after the addition was shifted into a higher molecular weight region that was well-resolved from the initial region, and there was no signal corresponding to the molecular weight of the polymer before the addition. Furthermore, when the polymer from such polymerizations was isolated with the active endgroup intact and redissolved in new solvent, the monomer concentration in the solution increased over time due to depolymerization (Figure 3). The limit that the depolymerization curve approached was essentially the identical concentration observed for the polymerization curve. Thus, the value that the curve in Figure 2 approached was the equilibrium monomer concentration for the polymerization, and the polymerization of *n*-hexyl isocyanate using organotitanium(IV) catalysts is fully reversible between monomer and polymer.

The occurrence of a monomer−polymer equilibrium explains the strong dependence of yield upon the initial monomer concentration of these polymerizations, because as the concentration of monomer approaches the equilibrium concentration for the polymerization, the amount of monomer that can be incorporated into polymer diminishes to zero. If the initial concentration of monomer is equal to the equilibrium monomer concentration, then no polymerization will occur. Several authors have suggested that polyisocyanates have a low ceiling temperature,[21] but ceiling temperature effects have never been observed directly in anionic polymerizations due to the preponderance of trimerization at higher reaction temperatures. Because trimerization does not occur in the organotitanium(IV)-catalyzed polymerizations, a ceiling temperature for polyisocyanates could be observed directly for the first time. The reversible nature of the polymerizations allowed us to measure the thermodynamic polymerization parameters for PHIC: $\Delta H_p = -8.5 \pm 0.5$ kcal mol$^{-1}$; $\Delta S_p = -27 \pm 1$ eu; $T_c = 43$ °C.[20]

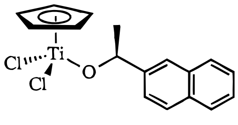
The Lewis acidity of the titanium center can be lessened by the replacement of a chloride ligand with a more electron donating and sterically bulkier ligand such as $\eta^5$-cyclopentadienyl (Cp). Polymerizations of *n*-hexyl isocyanate using catalysts **2**−**4** proceed in an analogous manner to those using **1**, although they are noticeably slower. The nature of the initiating ligand on the titanium center in catalysts **2**−**4** generally had no discernible effect upon its activity. The notable exception is that titanium phenoxides will not initiate polymerization. These catalysts, unlike **1**, can polymerize monomers possessing donor functional groups, such as 2-isocyanatoethyl methacrylate.[22] In general, we have found that catalysts **2**−**4** will polymerize most isocyanates, the exceptions being sterically bulky isocyanates (secondary and tertiary isocyanates), aryl isocyanates (the catalyst decomposes to a brown suspension), and isocyanates with enolizeable protons. As with polymerizations using **1**, polymerizations using catalysts **2**−**4** display a linear correspondence between molecular weight and the percent conversion[23] and monomer-to-initiator ratio (Molecular weight plots, as shown in Figure 1 for catalyst **1**, were obtained for the polymerization of *n*-hexyl isocyanate using catalysts **2**−**4**). The polydispersities of PHIC synthesized using catalysts **2**−**4** are typically lower than those using **1** (1.05−1.15 vs 1.1−1.2).

**Table 1.** Data for the Oligomerization of *n*-Hexyl Isocyanate Using Catalysts **5** and **6**

| catalyst | yield (%) | MW[b] | PDI[b] | oligomer $[\alpha]_D$[c] (deg) | endgroup contribution[d] (deg) |
|---|---|---|---|---|---|
| **5** | 60[a] | 4850 | 1.19 | 33 | 0.056 |
| **6** | 91 | 3340 | 1.16 | 21 | 0.018 |

[a] Catalyst had a limited solubility in the polymerization medium. [b] Determined by GPC calibrated relative to polystyrene standards. [c] In $CHCl_3$. [d] Optical rotation expected if all of the initiating ligand were present as the free alcohol.

With both classes of catalysts, the initiating ligand subsequently can be observed on the end of the polymer chain. For polymerizations using catalysts **1** and **2**, the 2,2,2-trifluoroethoxy endgroups are observed in the $^{19}F\{^1H\}$ NMR spectra of the resulting polymer samples ($\delta$ −74.8 ppm), with the intensity of the fluorine NMR signal being proportional to the molecular weight of the polymer. In addition to using fluorine labeling to demonstrate the presence of the initiating ligand on the end of the polymer chain, we labeled the initiating ligand with a chiral center. $CpTiCl_3OR$ derivatives with two chiral alcohols, (*R*)-(+)-α-methyl-2-naphthalene methanol, **5**, and (1*S*,2*R*,5*S*)-(+)-menthol, **6**, were prepared and used to oligomerize *n*-hexyl isocyanate. As shown in Table 1, the resulting oligomers were obtained in high yields, with narrow molecular weight distributions, and with sizable optical rotations. The optical rotations were in excess of what would be expected if all of the initiating alkoxide ligand were present as the free alcohol. Therefore, the optical rotations must be due to the initiating ligand, as an endgroup, exerting a stereochemical bias upon the conformation of the oligomer chain. Okamoto and co-workers[24] recently demonstrated that optically active amido endgroups had a far greater stereogenic influence upon the conformation of the polymer chain than alkoxide endgroups. Because monoamido derivatives of $CpTiCl_3$ are as equally easy to prepare as monoalkoxide derivatives, the use of $CpTiCl_2L$ catalysts represents an efficient method for the preparation of well-defined, end-functionalized, optically active isocyanate oligomers.



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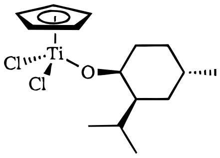

**6**

In fact, a polyisocyanate chain can be end-functionalized with just about any molecular structure imaginable, with the only stipulation being that the molecule contains no functional groups that will react with the titanium center. In addition to the aforementioned chiral alkoxides, we prepared $CpTiCl_3$ derivatives of two polymerizable alcohols, methyl α-(hydroxymethyl)-

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[21] (a) Reference 13. (b) Eromosele, I. C.; Pepper, D. C. *J. Polym. Sci., Polym. Chem.* **1987**, *25*, 3499. (c) Ivin K. J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 487.

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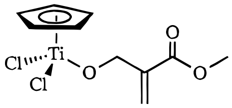
[24] Okamoto, Y.; Matsuda, M.; Nakano, T.; Yashima, E. *Polym. J. (Tokyo)* **1993**, *25*, 391.

acrylate, **7**, and *endo*/*exo*-5-norbornene-2-methanol, **8**. Both of these compounds are active catalysts for the polymerization of isocyanates and have been used to synthesize PHIC macromonomers. These titanium compounds might also be stitched together to form a macromolecule with pendant catalyst centers. Polyisocyanate chains could then be grown from the polymer to any desired length.



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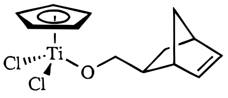

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**Living Character of the Polymerizations.** The microscopic (i.e., kinetic) behavior of a living polymerization is manifested in measurable, macroscopic characteristics of the polymerization and resulting polymer sample.[3] These include the following:[25] (1) qualitative conversion of the monomer into polymer with a first order dependence of the rate upon both catalyst and monomer concentration; (2) a linear correlation between the molecular weight of the polymer and the percent conversion of the polymerization; (3) a linear correlation between the molecular weight of the polymer and the monomer-to-initiator ratio of the polymerization; (4) the resulting polymer has a narrow polydispersity; (5) the living chain ends can be quantitatively functionalized; and (6) the living chain ends can be employed in the synthesis of block copolymers. Demonstration of one of these criteria, by itself, is not sufficient to establish the living character of the polymerization, because each criterion has its own particular caveats. However, demonstration of the group as a whole represents a strong case for a living polymerization.

For the organotitanium(IV)-catalyzed polymerization of isocyanates see the following:

(1) The polymerizations are quantitative because they proceed until they reach the equilibrium concentration of monomer. When polymerizations are conducted in bulk, isolated yields as high as 95% have been obtained. Also, the rate of polymerization displays a first order dependence upon both the catalyst concentration and monomer concentration (*vide infra*).

(2) The molecular weight of the growing polymer chains in polymerizations using catalysts **1**−**4** is linearly dependent upon the percent conversion of the polymerizations.

(3) As shown in Figures 1−4, the molecular weight of the isolated polymer is linearly dependent upon the monomer-to-initiator ratio.

(4) The polydispersity of polymers synthesized using catalysts **1**−**4** range from 1.05 to 1.2.

(5) Polymerizations using catalysts **2**−**4** can be endcapped quantitatively using carboxylic acid anhydrides. For example, when the initiating end of PHIC is fluorine labeled using a catalyst with a fluorine-containing initiating ligand (such as **2**) and then the polymerization is treated with trifluoroacetic anhydride, the $^{19}F\{^{1}H\}$ NMR spectrum of the resulting isolated, purified polymer shows two signals in a one-to-one integration ratio. One signal, with a chemical shift of −74.8 ppm, corresponds to that found for the 2,2,2-trifluoroethoxy initiating ligand, and the other, with a chemical shift of −70.5 ppm, corresponds to the trifluoroacetamido endcap.[26]

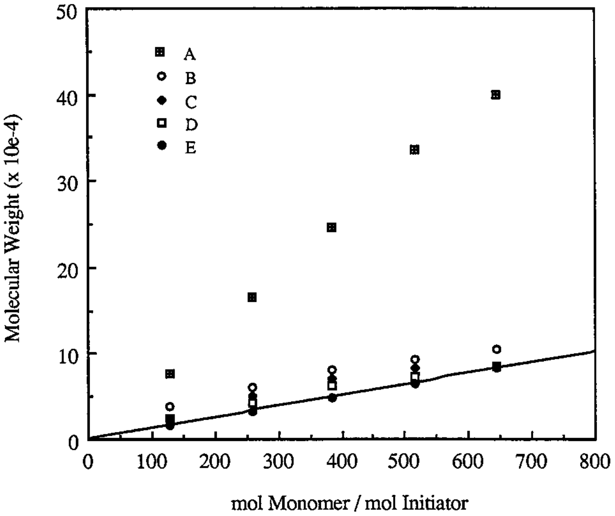

**Figure 1.** Plots of molecular weight, determined using various techniques, versus the monomer-to-initiator ratio for the polymerization of *n*-hexyl isocyanate using **1**. Legend: (A) Determined using GPC calibrated relative to polystyrene standards (since PHIC is a rigid polymer, it is expected that these molecular weight values will be inflated relative to the absolute molecular weights). (B) Determined using Ubbelhode viscometry using the Mark−Houwink constants measured by Teremoto, Aharoni, and co-workers in ref 44. (C) Determined using static light-scattering. (D) Determined using Ubbelhode viscometry using the Mark−Houwink constants measured by Berger and Tidswell in ref 45. (E) Expected molecular weights.

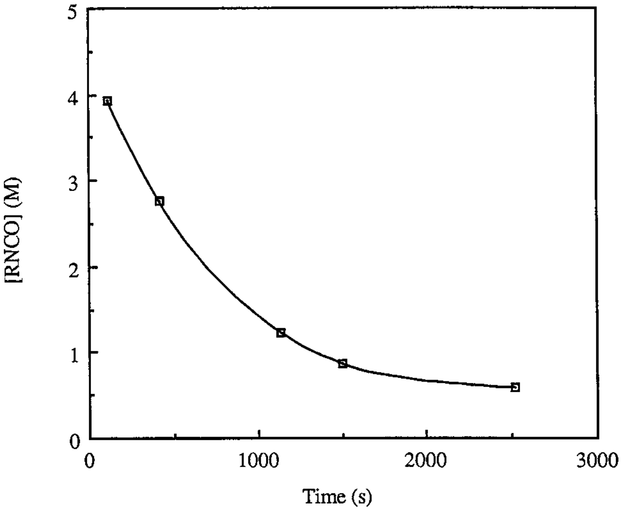

**Figure 2.** A plot of monomer concentration versus time for the polymerization of *n*-hexyl isocyanate using **1**.

(6) We have shown in GPC experiments that addition of a different isocyanate to a living polyisocyanate increases the molecular weight of the final copolymer relative to the intermediate polymer and that the intermediate homopolymer is not observed in the final copolymer.[20] We have also synthesized and characterized well-defined block copolymers between monoisocyanates and diisocyanates (Table 2).[27]

**Kinetics and Mechanism of Titanium(IV)-Catalyzed Polymerizations of Isocyanates.** Because these polymerizations are well-behaved and the polymerization technique, itself, is novel, we investigated the kinetics and mechanism of organotitanium(IV)-catalyzed isocyanate polymerizations. For these studies we chose to work primarily with catalysts **2**−**4**, because

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[25] For recent discussion of experimental criteria for living polymerizations, see: (a) Matyjaszewski, K. *Macromolecules* **1993**, *26*, 1787. (b) Penczek, S.; Kubisa, P.; Szymanski, R. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 77. (c) Quirk, R. P.; Lee, B. *Polym. Int.* **1992**, *27*, 359.

[26] Recently, Hatada and co-workers investigated endcapping reactions of *n*-butyl isocyanate polymerizations where **1** was used as the catalyst: Ute, K.; Asai, T.; Fukunishi, Y.; Hatada, K. *Polym. J. (Tokyo)* **1995**, *27*, 445.

[27] A complete account of the synthesis and polymerization of 1,2-diisocyanates will appear elsewhere: Patten, T. E.; Novak, B. M. Manuscript in preparation.

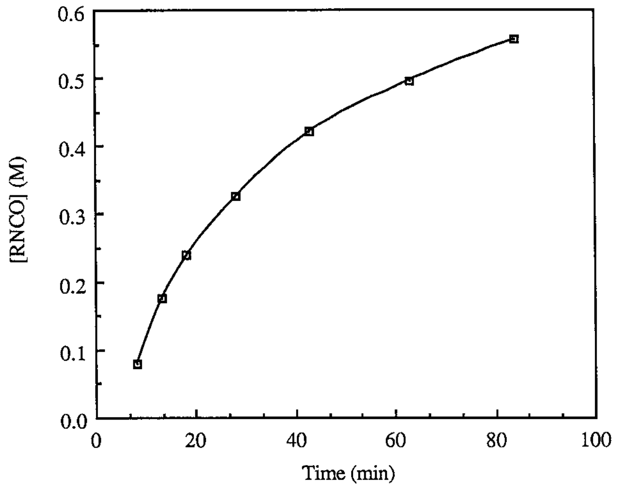


**Figure 3.** A plot of monomer concentration versus time for the depolymerization of active PHIC polymerized using **1**.

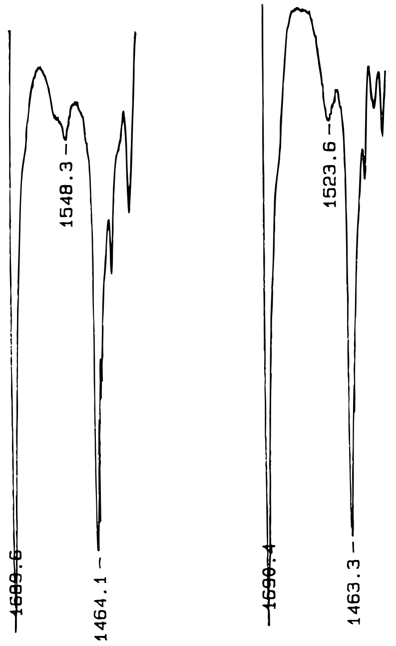


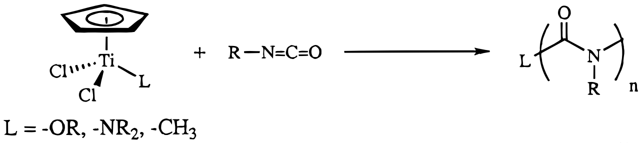
**Figure 4.** Regions (1700−1400 cm$^{-1}$) of the IR spectra taken of the active oligomerization of *n*-hexyl isocyanate using **3**. Left: before quenching with $CH_3OH$. Right: after quenching with $CH_3OH$.

**Table 2.** Experimental Data for the Block Copolymerization of *n*-Hexyl Isocyanate with 1,2-Diisocyanatopropane Using Catalyst **3**

| characterization | after addition of *n*-hexyl isocyanate to compd **3** | after addition of 1,2-diisocyanatopropane to the active PHIC block[b] |
|---|---|---|
| $M_n$ (GPC) | 6790 | 9960 |
| $M_w/M_n$ (GPC) | 1.1 | 1.2 |
| solubility in hexanes[a] | yes | no[c] |
| solubility in $CHCl_3$[a] | yes | yes |

[a] PHIC is soluble in hexanes and $CHCl_3$, whereas poly(1,2-diisocyanatopropane) is insoluble in both of these solvents. [b] Neither a shoulder nor a peak corresponding to the molecular weight of the PHIC block was observed in the GPC chromatogram of the final product. The molecular weight distribution was unimodal. [c] Extraction of the final block copolymer with hexanes yielded no PHIC.

polymerizations using these compounds occur at a rate that is convenient for analysis using IR techniques. In each of these polymerizations the initiating ligand is subsequently observed on the end of the purified polymer chains (*vide supra*), which indicates that initiation of the polymerization occurs by the insertion of an isocyanate into the titanium-initiating ligand bond (eq 3). Similar insertions of isocyanates into metal−ligand bonds of small molecule titanium(IV) and zirconium(IV) complexes have been observed as well.[28,29]

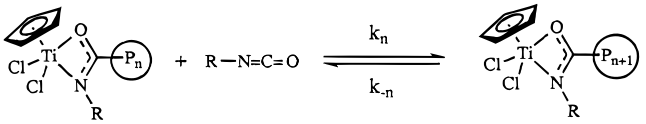


L = -OR, -NR$_2$, -CH$_3$

(3)

An IR spectrum of an active oligomerization of *n*-hexyl isocyanate using catalyst **3** showed, in addition to other peaks, a medium-intensity band at 1548 cm$^{-1}$ (Figure 4). The monomer, starting catalyst, solvent, and the resulting polymer showed no absorptions in the region in which this band appears, 1684−1468 cm$^{-1}$, so this band was due to a new species formed in the polymerization. Upon addition of methanol to the solution this band disappeared, and a new band at 1524 cm$^{-1}$ appeared (Figure 4). The intensites of the 1548 cm$^{-1}$ band and the 1524 cm$^{-1}$ band varied inversely with the initial monomer-to-initiator ratio of the polymerization. From this evidence we concluded that these IR absorptions were due to the active and terminated endgroups of the polymerization.

Confirmation of this assignment and information concerning the structure of the endgroup was obtained from literature reports of titanium-isocyanate insertion compounds. The 1548 cm$^{-1}$ band corresponds to a region of IR stretching frequencies found for titanium amidates. For example, the IR spectrum of the tetrainsertion compound of tetrakisdimethylamidotitanium with phenyl isocyanate[29a] shows an absorption at 1555 cm$^{-1}$ assigned to the stretching frequency of the O−C−N unit of the $\eta^2$-ureidate ligands. The IR spectra of the monoinsertion derivatives of $Cp_2Ti(\eta^3\text{-allyl})$[29d] and $Cp_2TiCH_3$[29c] with phenyl isocyanate showed absorptions at 1536 and 1550 cm$^{-1}$, respectively, assigned to the vibrations of the O−C−N unit of the $\eta^2$-amidate ligand. With each of these three compounds, the ligands could be protonated off the titanium center using $H_2O$ or an alcohol to give essentially quantitative yields of the corresponding urea or amide derivatives. Because the IR stretch observed for the active oligomer is very similar to the data reported for these literature compounds, we believe that the bischloro-$\eta^5$-cyclopentadienyltitanium(IV)-$\eta^2$-amidato structure, as shown in eq 4, is an accurate representation of the structure of the active propagating endgroup in these polymerizations.



(4)

The 1524 cm$^{-1}$ band of the quenched oligomer is within the region normally found for the amide II band of secondary amides in dilute solution, 1550−1510 cm$^{-1}$.[30] For example, IR spectra of dilute chloroform solutions of *N*-methyl acetamide and trimethylurea showed amide II bands at 1534 and 1539 cm$^{-1}$, respectively. Thus, termination of the polymerization,

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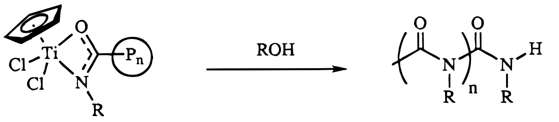
(28) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 654.

(29) (a) Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc. (A)* **1970**, 2550. (b) Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *222*, 79. (c) Klei, E.; Telgen, J. H.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *209*, 297. (d) Klei, E.; Teuben, J. H.; De Liefde Meijer, H. J.; Kwak, E. J.; Bruins, A. P. *J. Organomet. Chem.* **1982**, *224*, 327.

(30) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley and Sons: New York, 1981; pp 124−127.

through addition of an alcohol, occurs via protonation of the amidate endgroup from the metal center to yield the corresponding secondary amide endgroup and titanium alkoxide compound (eq 5). The excess alcohol used in the termination



(5)

of these polymerizations as well as any adventitious water can react further with the free titanium alkoxide compound to form various other titanium species, so the catalyst utilized in these polymerizations is neither recovered nor recycled.

The reaction of particular interest is the propagation step of the polymerization, because there is little knowledge concerning the mechanism of multiple insertions of isocyanates into metal-ligand bonds. Equation 4 shows the general propagation step of the polymerization where the forward and reverse processes can occur. In this step, either the carbon−nitrogen or carbon−oxygen double bond of an isocyanate adds accross the titanium−nitrogen bond of the $\eta^2$-amidate endgroup. This particular addition regiochemistry is required in order to obtain the amide-repeat-unit structure of the polymer. The resulting species must then rearrange in a fast process to yield the observed $\eta^2$-amidate endgroup structure. The rate law for this reaction is shown in eq 6. This expression can be simplified and then integrated after using the equilibrium expression for the polymerization ($K_{eq} = k_1/k_{-1} = 1/[\text{monomer}]_{eq}$) and assuming that (1) the active chain ends on polymer molecules of differing chain length show the same reactivity[31] and (2) the concentration of active chain ends equals the initial concentration of catalyst, which is true for a living polymerization (eq 7).

$$\frac{-\mathrm{d}[\mathrm{RNCO}]}{\mathrm{d}t} = [\mathrm{RNCO}]\left(\sum_{n=\mathrm{MW}_1}^{\mathrm{MW}_x} k_n[\mathrm{CpTiCl_2\text{-}P}_n]\right) - \left(\sum_{n=\mathrm{MW}_1}^{\mathrm{MW}_x} k_{-n}[\mathrm{CpTiCl_2\text{-}P}_n]\right) \quad (6)$$

$$\ln\left(\frac{[\mathrm{RNCO}] - [\mathrm{RNCO}]_{eq}}{[\mathrm{RNCO}]_0 - [\mathrm{RNCO}]_{eq}}\right) = -k_1[\text{catalyst}]t \quad (7)$$

If this integrated rate law is consistent with the actual mechanism of propagation, a plot of the logarithmic concentration function of the experimental data versus time should fit a straight line with a negative slope of the magnitude of the product of the catalyst concentration and the forward macroscopic rate constant. The observed rate of the polymerization should also exhibit a first-order dependence upon catalyst concentration. Furthermore, eq 7 should also hold true for the kinetics of depolymerization, because the derived rate law for depolymerization is identical to this equation. We took the complete set of polymerization and depolymerization data shown in Figures 2 and 3 and applied eq 7. The resulting plots are shown in Figure 5, and the data in both plots could be fitted to least-squares lines with $R^2$ values of 0.986 and 0.997 for the full 4−5 measured half-lives. The observed rate constants for these and several other polymerizations/depolymerizations using **1** are shown in Table 3. When the concentration of catalyst is factored out, the forward rate constants obtained for each experiment were, within experimental error, the same. The kinetics of several polymerizations of $n$-hexyl isocyanate using **2** at various concentrations were monitored, and a plot of the observed rate constants as a function of catalyst concentration was fitted with a least-squares line. The slope of the plot yielded a forward rate constant of 8.5 × $10^{-4}$ mol $L^{-1}$ $s^{-1}$ (Figure 6). The depolymerization rate constant, 3.8 × $10^{-4}$ $s^{-1}$ was calculated using the equilibrium expression for the polymerization. The above kinetics measurements illustrate that these polymerizations are well-behaved, living systems and are consistent with the derived rate law.

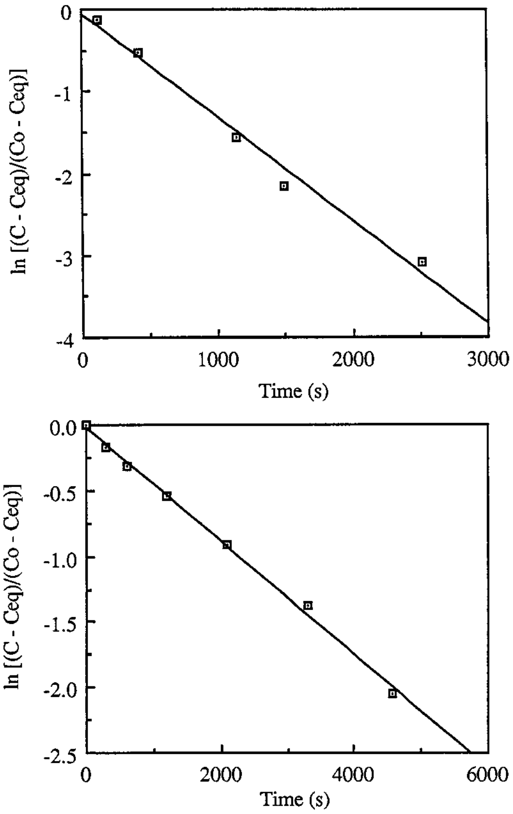


**Figure 5.** Plots of the kinetic data from Figures 2 and 3 after applying eq 7. Above: polymerization. Below: depolymerization.

**Table 3.** Kinetic Data for the Polymerization and Depolymerization of $n$-Hexyl Isocyanate Using **1**

| reaction | [catalyst] (M) | $k_{obs}$ ($M^2$ $s^{-1}$) | $k_1$ (M $s^{-1}$) |
|---|---|---|---|
| polymerization | 0.0825 | 1.3 × $10^{-3}$ | 1.6 × $10^{-2}$ |
| | 0.0853 | 1.1 × $10^{-3}$ | 1.3 × $10^{-2}$ |
| | 0.0841 | 9.0 × $10^{-4}$ | 1.1 × $10^{-2}$ |
| | 0.0504 | 7.8 × $10^{-4}$ | 1.5 × $10^{-2}$ |
| | 0.0304 | 9.4 × $10^{-4}$ | 3.1 × $10^{-2}$ |
| depolymerization | 0.0306 | 5.2 × $10^{-4}$ | 1.7 × $10^{-2}$ |
| | 0.0484 | 4.3 × $10^{-4}$ | 9.0 × $10^{-3}$ |

To quantify the effect of the ligand environment upon the activity of the catalyst, several polymerizations were conducted using identical concentrations of several different catalysts: **1**; **2**; $\mathrm{Cp^*TiCl_2OCH_2CF_3}$ [Cp* = $\eta^5$-pentamethylcyclopentadienyl], **9**; and $\mathrm{Cp_2TiCl_2OCH_2CF_3}$, **10**. There was an order-of-magnitude decrease in the rate of polymerization when one of the ligands on the titanium center was varied from Cl to Cp to Cp* ($k_{obs}$ decreased from 7.8 × $10^{-4}$ to 3.8 × $10^{-5}$ to 3.3 × $10^{-6}$ $\mathrm{mol^2}$ $L^{-2}$ $s^{-1}$, respectively). With **10** the rate of polymerization was too slow for an accurate measurement. These data confirm the qualitative observations discussed earlier that increasing steric bulk about the metal center and increasing electron donation to the metal center from the ligands reduces the activity of the titanium catalyst.

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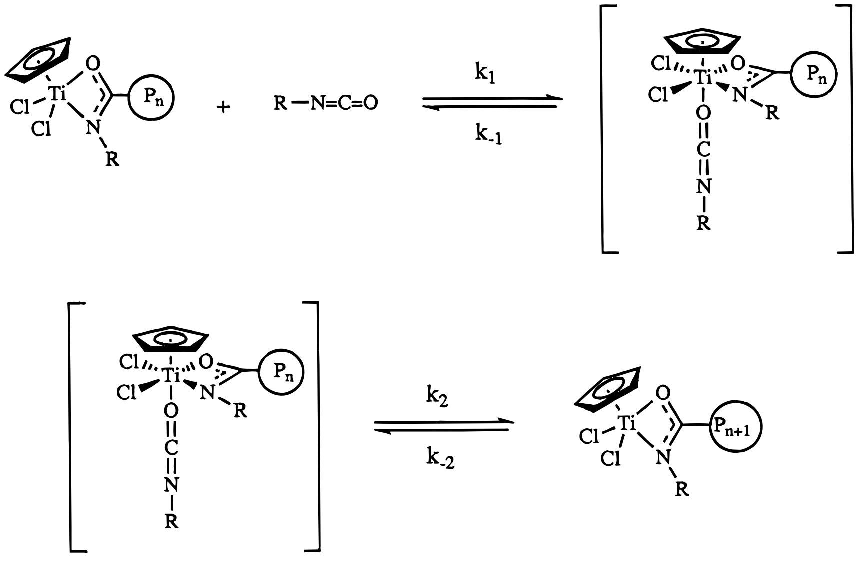
(31) Szwarc, M. *Advances in Polymer Science*; Springer-Verlag: New York, 1983; Vol. 49, pp 15−30 and 79−81.

**Scheme 1**



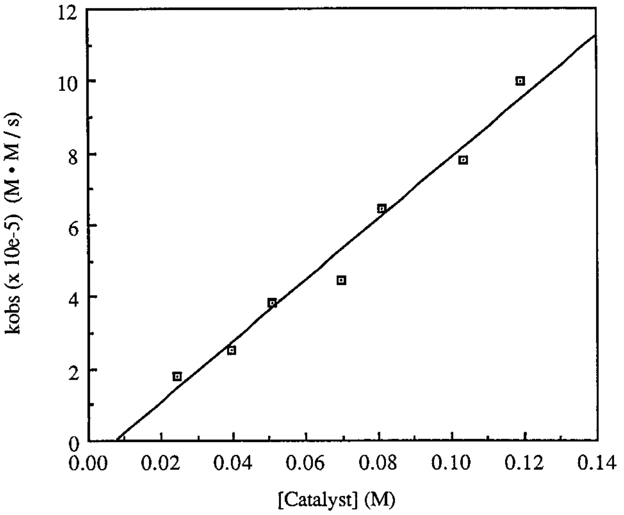


**Figure 6.** A plot of $k_{\mathrm{obs}}$ versus catalyst concentration for polymerizations of *n*-hexyl isocyanate using **2**.

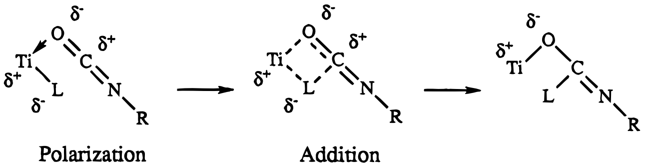
One issue that remains open about the polymerization mechanism is whether or not a discreet monomer−catalyst complex exists along the reaction coordinate. A propagation mechanism can be written where precoordination of the monomer occurs before the insertion step (Scheme 1, assuming oxygen coordination). The simplified rate expression is shown in eq 8. Manual integration of this equation does not yield a

$$\frac{-\mathrm{d}[\mathrm{RNCO}]}{\mathrm{d}t} = [\mathrm{catalyst}]\frac{k_1 k_2[\mathrm{RNCO}] - k_{-1}k_{-2}}{k_{-1} + k_2 + k_{-2} + k_1[\mathrm{RNCO}]} \qquad (8)$$

simple rate law that can be plotted, so numeric integration would be necessary to fit the data. An equation with four variables could most likely be minimized to fit the data, so other methods are necessary to distinguish between the two possible mechanisms. The chemical behavior of $\mathrm{CpTiCl_2L}$ complexes was used to gain insights into which of the two mechanisms is more likely.

If a coordination intermediate occurs along the mechanistic pathway, then the isolation of $\mathrm{CpTiCl_2L}$ adducts with Lewis bases should be possible. However, no monodentate ether, amine, or phosphine complex of $\mathrm{CpTiCl_3}$ has ever been prepared, and stable Lewis base adducts have only been isolated and characterized using very strong chelating donor ligands such as 2,2′-bipyridyl[32] and bisdimethylphosphinoethane.[33] The reluctance of these compounds to coordinate donor ligands suggests that the interaction between the titanium center and the isocyanate molecule during propagation must be weak. Instead of through formal coordination, the isocyanate molecule may insert into the metal−ligand bond via a bifunctional activation mechanism.[28,34] In this process, an empty orbital on the highly electron-deficient titanium center can accept electron density from the isocyanate group and polarize the carbon−oxygen or carbon−nitrogen double bond. The metal−ligand bond of interest is polarized in the opposite sense, and therefore nucleophilic addition of the ligand onto the isocyanate group can be viewed as a concerted addition (Scheme 2, assuming oxygen coordination). Instead of the deep potential well of a formal coordination complex, such a species would be a transition state or a very shallow potential well along the reaction coordinate. Carbon dioxide, which is isoelectronic with an isocyanate, has been shown to undergo this type of bifunctional activation addition in its reactions with simple bases and inorganic complexes.[34] This type of addition would be consistent with either mechanism and kinetic rate law.

**Scheme 2**



The possible insertion mechanisms discussed here can be viewed as a spectrum where at one end a formal coordination complex intermediate is formed, and at the other end the isocyanate undergoes a concerted [2 + 2] addition across the metal−ligand bond with no prerequisite interaction with the metal center. In light of the reluctance of $\mathrm{CpTiCl_2L}$ complexes to coordinate Lewis bases and the effects of steric bulk and electrophillicity of the metal center upon the rate of polymer-

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[32] Clark, R. J. H.; Stockwell, J. A.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1976**, 120.

[33] Hughes D. L.; Leigh, G. J.; Walker, D. G. *J. Organomet. Chem.* **1988**, *355*, 113.

[34] (a) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 792. (b) Dennard, A. E.; Williams, R. J. P. *Transition Metal Chemistry*; Carlin, R. L., Ed.; Marcel Dekker: New York, 1966; Vol. 2, pp 123−164. (c) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082.

ization, it seems most probable that the actual mechanism lies closer to the latter side of the spectrum.

## Conclusion

A living organotitanium(IV)-catalyzed polymerization of isocyanates was developed. A titanium trichloride alkoxide, **1**, was found to polymerize *n*-hexyl isocyanate to high yields and without the formation of cyclic trimer; however, polymerizations using **1** were inhibited by the presence of donor solvents or monomers possessing donor groups. Compounds **2**−**4** were found to polymerize isocyanates in the presence of donor solvents and isocyanates possessing donor functional groups, activated olefins, and strained olefins. The activity of the organotitanium(IV) catalysts decreased with increasing steric bulk about the metal center and increasing electron donation to the metal center from the ligands, and only polymerizations using catalysts **1**−**4** gave high yields of polymer within an experimentally practical time period. The nature of the initiating ligand on the titanium center in catalysts **2**−**4** had no detectable effect upon the activity of the catalyst, and both fluorine-labeled and chiral initiating ligands were detected on the end of the polymer chain using $^{19}$F NMR spectroscopy and polarimetry, respectively.

The polymerization of *n*-hexyl isocyanate using organotitanium(IV) compounds is living. Several experiments support this conclusion. The PDIs of PHIC synthesized using catalysts **1**−**4** were found to range from 1.05 to 1.2. The molecular weight of the polymer formed in polymerizations of *n*-hexyl isocyanate using catalysts **1**−**4** varied linearly as a function of the monomer-to-initiator ratio and the percent conversion of the polymerization. Polymerizations using **2** can be endcapped quantitatively, and well-defined block copolymers can be synthesized using catalysts **1**−**4**.

Polymerizations of isocyanates using organotitanium(IV) compounds were found to be completely reversible between monomer and polymer, enabling the determination of the thermodynamic parameters of PHIC. The kinetics of polymerizations using a wide variety of organotitanium compounds were measured. For the series of catalysts **1**, **2**, and **9**, the observed rate constants for polymerizations conducted under identical conditions decreased by an order of magnitude corresponding with each increase in the steric bulk and electron-donating capability of the spectator ligand. The kinetics for polymerizations using catalysts **1** and **2** were first-order in both monomer and catalyst. The active endgroup of a polymerization using **3** was observed using IR spectroscopy, and the frequency of the IR stretch was consistent with an $\eta^2$-amidate endgroup structure. Finally, the kinetic data for the polymerization of *n*-hexyl isocyanate and the known chemistry of $CpTiCl_2L$ compounds were found to be consistent with a propagation step that occurs via a bifunctional activation mechanism.

## Experimental Section

**General Procedures and Characterizations.** All manipulations involving air- and moisture-sensitive compounds were carried out under argon atmospheres using standard Schlenk techniques. Solids and monomers were transferred in an argon-filled Vacuum Atmospheres HE533 Dri Lab with attached HE493 Dri Train.

$^1$H and $^{13}$C{$^1$H} NMR spectra were determined at 400 and 100 MHz, respectively, using a Bruker AM-400 or AMX-400 FT NMR spectrometer or at 500 and 125 MHz, respectively, using a Bruker AM-500 FT NMR spectrometer. $^1$H NMR spectra were determined at 250 MHz on a superconducting spectrometer constructed in the UC Berkeley NMR Laboratory, equipped with a Cryomagnets, Inc. magnet and a Nicolet Model 1280 data collection system. $^{19}$F{$^1$H} NMR spectra were determined at 376 MHz using the Bruker AM-400 spectrometer. Chemical shifts for $^1$H spectra are reported in units of $\delta$ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to a selected residual proton signal of the solvent: $CDCl_3$, 7.25 ppm, singlet; toluene-$d_8$, 2.09 ppm, quintet; benzene-$d_6$, 7.15 ppm, broad. Significant $^1$H NMR data are tabulated in order: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broadened signal), coupling constant(s) in Hertz, and number of protons. Chemical shifts for $^{13}$C{$^1$H} spectra are reported in units of $\delta$ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to a selected carbon resonance of the solvent employed: $CDCl_3$, 77.0 ppm, triplet; toluene-$d_8$, 20.4 ppm, septet; benzene-$d_6$, 128.0 ppm, triplet. Chemical shifts for $^{19}$F{$^1$H} NMR spectra are reported in units of $\delta$ (ppm), negative values indicating shifts upfield of $CFCl_3$, and are referenced to α,α,α-trifluorotoluene internal standard: −63.72 ppm. Infrared spectra were determined using a Perkin-Elmer 1600 series FTIR. Polarimetry was performed using a Perkin-Elmer 141 polarimeter ($\lambda$ = 589 nm). Melting points were determined using an Electrothermal capillary melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory operated by the College of Chemistry, University of California, Berkeley, CA.

**Polymer Characterizations.** Gel permeation chromatography (GPC) was performed using a Hewlett/Packard 1050 series liquid chromatograph pump equipped with a HP Model 1047 refractive index detector and a HP model 3396A integrator. Separations were effected by $10^5$, $10^4$, $10^3$, and 500 Å Waters Ultrastyragel columns and molecular weights were calibrated relative to polystyrene standards (Scientific Polymer Products, Inc.): Mobile phase: $CHCl_3$ or THF; flow rate, 1 mL min$^{-1}$. Light-scattering in the tandem GPC/light-scattering experiments was performed using a Wyatt Technology Dawn Model F Multiangle Photometer. Measurements of $(\delta n/\delta c)_{T,P}$ were performed using a Chromatics KMX-16 Refractometer. Static light-scattering (SLS) measurements were performed using a Brookhaven Instruments-(BI)-9000 correlator and BI-200SM goniometer driven by BI-ZP software for automated acquisition and analysis of SLS data. Calibration to absolute intensities was performed using toluene standards. Thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer PC Series TGA7: scanning rate = 10 °C min$^{-1}$, atmosphere = nitrogen. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer PC series DSC.

**Reagents.** Solvents were purified as follows: toluene, benzene, hexanes, and tetrahydrofuran (THF) were distilled from Na/benzophenone. Isocyanate monomers were distilled from $CaH_2$ and stored under an argon atmosphere. Methylene chloride ($CH_2Cl_2$) and triethylamine ($Et_3N$) were distilled from $CaH_2$. *endo*/*exo*-5-Norbornene-2-methanol was distilled from $CaH_2$ under vacuum and stored under an argon atmosphere. (*R*)-(+)-α-Methyl-2-naphthalene methanol and (1*S*,2*R*,5*S*)-(+)-menthol were sublimed under vacuum and stored in a drybox. 2,2,2-Trifluoroethanol was vacuum transferred from $MgSO_4$ that had been dehydrated by heating at 150 °C under a high dynamic vacuum for 2 days. $(CH_3)_3SiN(CH_3)_2$ was obtained from Huls America, fractionally distilled, and stored under an argon atmosphere. Titanium(IV) chloride was stirred over copper turnings for 24 h and distilled through an all-glass apparatus. Catalyst **1** was prepared according to the procedure of Paul and co-workers.[35] Methyl α-(hydroxymethyl)acrylate was prepared according to the procedure of Mathias and co-workers.[36] $Cp^*TiCl_3$ was prepared according to the procedure of Llinás and co-workers.[37] Unless specified otherwise, all other reagents were obtained from Aldrich Chemical Co. and used without further purification.

**Experimental Procedures and Characterizations. $TiCl_3OCH_2CF_3(THF)_2$.** To a 25 mL Schlenk flask containing 5 mL of $CH_2Cl_2$ was added via syringe 1.80 mL (3.11 g, 16.4 mmol) of $TiCl_4$. The flask was placed in an ice/water bath, and then 1.00 mL (1.37 g, 13.7 mmol) of $HOCH_2CF_3$ was added via syringe. The solution was stirred for 1 h, and then the flask was fitted with a reflux condenser. The solution

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(35) Paul, R. C.; Sharma, P.; Gupta, P. K.; Chadha, S. L. *Inorg. Chim. Acta* **1976**, *20*, 7.

(36) (a) Mathias, L. J.; Kusefoglu, S. H. *Macromolecules* **1987**, *20*, 2041. (b) Mathias, L. J.; Kusefoglu, S. H.; Kress, A. O. *Macromolecules* **1987**, *20*, 2327.

(37) Llinás, G. H.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37.

was stirred and heated at reflux under argon overnight. The next day volatile materials were removed under vacuum to leave 1.40 g (40% yield) of a white powder: $^1$H NMR (250 MHz, toluene-$d_8$) $\delta$ 3.91 (br).

Next, 1.31 g of this powder was weighed into a 100 mL Schlenk flask. Via cannula, 25 mL of $CH_2Cl_2$ was added, and the flask was fitted with a pressure-equalizing addition funnel. The addition funnel was charged with 25 mL of $CH_2Cl_2$ and 2.00 mL of THF. The flask was cooled to 0 °C using and ice/water bath, and the THF solution was added dropwise to the solution of **1**. After complete addition, the amount of solvent was reduced to approximately 10 mL under vacuum. Via cannula 80 mL of hexanes was layered onto the solution, and the flask was tightly closed and placed in a $-40$ °C freezer. Over a 2 day period colorless crystals formed. The supernatant was removed, and solvents were removed from the crystals under vacuum leaving 1.67 g (81% yield) of colorless crystals: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.90 (br, 2H), 3.9 br, 8 H), 1.30 (br, 8H); $^{19}$F{$^1$H} NMR (376 MHz, $CDCl_3$) $\delta$ $-75.66$; IR (thin film) 2985 (m), 2909 (m), 1458 (w), 1279 (s), 1150 (vs), 1039 (w), 1010 (m), 952 (m), 920 (w), 856 (m), 774 (sh), 716 (m), 628 (w) cm$^{-1}$. Anal. Calcd for $C_{10}H_{18}Cl_3F_3O_3Ti$: C, 30.22; H, 4.56; N, 0.00. Found: C, 31.50; H, 4.47; N, 0.02.

**$CpTiCl_3$.** The following synthesis is a modification of the procedure of Gorsich.[38] In a drybox, a 250 mL three-necked flask with a large egg-shaped stir bar was charged with 10.0 g (40.3 mmol) of $Cp_2TiCl_2$. The flask was closed, taken out of the drybox, and connected to a Schlenk line. A reflux condenser with a joint-to-hose adapter was attached, and via cannula 100 mL of toluene was added to the flask. The mixture was stirred, while the flask was cooled to 0 °C using an ice−water bath. Then 13.5 mL (23.4 g, 123 mmol) of $TiCl_4$ was added to the slurry via syringe. The ice bath was removed, and the flask was immersed in an oil bath. The oil was heated to 135−140 °C so the toluene reached reflux, and over time the $Cp_2TiCl_2$ dissolved to form a deep red solution. The reaction was stirred and heated at reflux for 6 h.

After the reflux time was complete, the heat source was removed, and stirring was stopped. The reaction mixture was left to cool overnight, and as the solution cooled orange crystals of $CpTiCl_3$ formed. The supernatant was removed via cannula, and volatile materials were removed from the product under vacuum, leaving 13.4 g (76% yield) of crude product. A portion of the crude product (4.25 g) was transferred to a vacuum sublimation apparatus, and sublimation at 90 °C and 0.01 Torr afforded 3.90 g (92% recovery) of orange crystals: mp = 212−214 °C (lit. 208−211 °C);[38] $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.03 (s) (lit. ($CH_3CN$) 7.25);[39] $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 123.40; IR (thin film) 3112 (m), 2971 (w), 2856 (w), 1880 (w), 1801 (w), 1703 (w), 1436 (s), 1066 (w), 1019 (m), 843 (m), 790 (sh) cm$^{-1}$.

**$CpTiCl_2OCH_2CF_3$, 2.** In a 50 mL Schlenk flask, $CpTiCl_3$ (0.346 g, 1.58 mmol) was dissolved in 10 mL of benzene. Then a solution of 0.115 mL (1.58 mmol) of $CF_3CH_2OH$ and 0.220 mL (1.58 mmol) of $Et_3N$ in 10 mL of benzene was added dropwise via a pressure-equalizing addition funnel. A white precipitate of $Et_3NH^+Cl^-$ formed. The solution was stirred for 2 h and then filtered. Benzene was removed under vacuum, and the product (0.384 g, 86%) was transferred to a sublimation apparatus. Sublimation at 80 °C and 0.01 Torr afforded 0.317 g (71% yield) of yellow crystals: mp = 87.5−90 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.81 (s, 5H), 4.79 (q, 2H, $J_{H-F} = 8.3$ Hz) (lit. ($CCl_4$) 6.85 (s), 4.75 (q));[40] $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 122.88 (q, $J_{C-F} = 279$ Hz), 121.51, 77.46 (q, $J_{C-C-F} = 36$ Hz); $^{19}$F{$^1$H} NMR (376 MHz, $CDCl_3$) $\delta$ (ppm) $-72.5$; IR (thin film) 3116 (s), 2934 (w), 2869 (w), 1872 (w), 1793 (w), 1696 (w), 1459 (sh), 1444 (s), 1398 (w), 1365 (m), 1282 (vs), 1154 (vs), 1065 (w), 1026 (m), 1016 (m), 956 (m), 937 (sh), 833 (s), 784 (w), 724 (m), 668 (w), 627 (m) cm$^{-1}$. Anal. Calcd for $C_7H_7Cl_2F_3OTi$: C, 29.72; H, 2.49; N, 0.00. Found: C, 30.11; H, 2.49; N, 0.01.

**$CpTiCl_2N(CH_3)_2$, 3.** In a 10 mL Schlenk flask, $CpTiCl_3$ (0.723 g, 3.48 mmol) was dissolved in 5 mL of THF. Then 0.550 mL (3.48 mmol) of $(CH_3)_3SiN(CH_3)_2$ was added via syringe. The solution turned deep red and was stirred for 24 h. THF and volatile products were removed under vacuum, and the product (0.615 g, 79%) was transferred to a sublimation apparatus. Sublimation at 90 °C and 0.01 Torr afforded 0.521 g (66% yield) of orange crystals: mp = 121−123 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.61 (s, 5H), 3.82 (s, 6H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 188.44, 52.11; IR (thin film) 3125 (m), 3101 (m), 3004 (w), 2961 (m), 2903 (m), 2878 (m), 2838 (w), 2797 (w), 2787 (w), 1863 (vw), 1786 (vw), 1684 (vw), 1448 (sh), 1438 (m), 1427 (m), 1406 (w), 1366 (w), 1244 (w), 1133 (w), 1072 (vw), 1044 (w), 1028 (m), 1020 (m), 913 (s), 832 (s), 784 (sh), 707 (vw) cm$^{-1}$. Anal. Calcd for $C_7H_{11}Cl_2NTi$: C, 36.88; H, 4.86; N, 6.14. Found: C, 36.49; H, 4.69; N, 6.02.

**$CpTiCl_2CH_3$, 4.** This compound was prepared using a modification of the procedure of Erskine et al.[41] In a 50 mL Schlenk flask, $CpTiCl_3$ (0.503 g, 2.29 mmol) was dissolved in 25 mL of THF. The flask was cooled to 0 °C with an ice bath, and then 0.760 mL of a 3.0 M solution of MeMgCl in THF was added dropwise via syringe over a 1 h period. THF was then removed under vacuum. The solid was extracted with 25 mL of benzene for 1 h and filtered. Benzene was removed under vacuum, and the product (0.276 g, 60%) was transferred to a sublimation apparatus. Sublimation at 50 °C and 0.01 Torr onto a dry ice/isopropyl alcohol cold finger afforded 0.157 g (34% yield) of orange crystals: mp = steadily decomposed upon heating; $^1$H NMR (400 MHz, toluene-$d_8$) $\delta$ (ppm) 5.90 (s, 5H), 1.71 (s, 3H) (lit. (benzene-$d_6$) 5.87, 1.74);[41] $^{13}$C{$^1$H} NMR (100 MHz, toluene-$d_8$) $\delta$ (ppm) 118.89, 79.65; IR (thin film) 3104 (s), 2974 (m), 2868 (m), 1863 (w), 1778 (w), 1682 (w), 1437 (s), 1389 (w), 1438 (w), 1389 (w), 1094 (sh), 1066 (m), 1019 (m), 910 (w), 835 (s), 792 (m), 708 (w) cm$^{-1}$. Anal. Calcd for $C_6H_8Cl_2Ti$: C, 36.23; H, 4.05; N, 0.00. Found: C, 35.75; H, 3.87; N, 0.00.

**$Cp_2TiClOCH_2CF_3$, 10.** To a mixture of 0.500 g (2.01 mmol) of $Cp_2TiCl_2$ in 50 mL of benzene was added 0.600 mL (4.30 mmol) of $Et_3N$. The mixture was heated at 60 °C until all the solid dissolved. The resultant bright red solution was then treated with 0.140 mL (1.92 mmol) of $CF_3CH_2OH$. After several minutes the solution became bright orange, and a white precipitate formed. The mixture was heated at 60 °C for 1 h and then heating was discontinued. The mixture was allowed to stir for an additional 10 h at room temperature, after which it was filtered. Benzene was removed under vacuum to give 0.487 g (78% yield) of an orange solid: mp = 81−82.5 °C; $^1$H NMR (400 MHz, benzene-$d_6$) $\delta$ (ppm) 5.76 (s, 10H), 4.26 (q, 2H, $J_{H-F} = 9.0$ Hz); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 124.33 (q, $J_{C-F} = 279$ Hz), 117.47, 76.62 (q, $J_{C-C-F} = 34$ Hz); $^{19}$F{$^1$H} NMR (376 MHz, benzene-$d_6$) $\delta$ (ppm) $-76.1$; IR (thin film) 3100 (m), 2897 (m), 2852 (m), 1873 (vw), 1782 (vw), 1681 (vw), 1630 (vw), 1444 (m), 1365 (w), 1280 (s), 1145 (s), 1015 (m), 952 (m), 888 (m), 857 (m), 817 (s), 592 (w) cm$^{-1}$.

**$Cp^*TiCl_2OCH_2CF_3$, 9.** In a 50 mL Schlenk flask, $Cp^*TiCl_3$ (0.505 g, 1.75 mmol) was dissolved in 20 mL of THF; via syringe 0.241 mL (1.73 mmol) of $Et_3N$ was added. Then a solution of 0.126 mL (1.73 mmol) of $CF_3CH_2OH$ in 10 mL of THF was added dropwise via a pressure-equalizing addition funnel. A white precipitate of $Et_3NH^+Cl^-$ formed, and the red solution turned bright orange. The solution was stirred for 3 h and then filtered. Removal of solvent under vacuum yielded 0.457 g (75% yield) of an orange solid: $^1$H NMR (400 MHz, toluene-$d_8$) $\delta$ (ppm) 4.37 (q, 2H, $J_{H-F} = 8.6$ Hz), 1.90 (s, 15H); $^{13}$C{$^1$H} NMR (100 MHz, toluene-$d_8$) $\delta$ (ppm) 133.38, 74.18 (q, $J_{C-C-F} = 36$ Hz), 12.71 ($CF_3$ not found).

**Bischloro-$\eta^5$-cyclopentadienyl-(*R*)-α(+)-1-(2-napthyl)ethoxy Titanium(IV), 5.** This compound was prepared using the same procedure for the synthesis of **2**. The quantities of reagents used were 0.501 g (2.28 mmol) of $CpTiCl_3$, 0.394 g (2.29 mmol) of (*R*)-(+)-α-methyl-2-naphthalene methanol, 0.320 mL (0.232 g, 2.30 mmol) of $Et_3N$, and 2 × 25 mL of benzene. Yield: 0.682 g (84%) of a yellow solid. The crude product was recrystallized from a solution of THF/hexanes to yield 0.359 g (53% recovery) of yellow needle-like crystals: mp = 145−147 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.88 (m, 4H), 7.52 (m, 3H), 6.54 (s, 5H), 5.95 (q, $J = 6.4$ Hz, 1H), 1.72 (d, $J = 6.5$ Hz), 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 140.72, 133.10, 128.75, 128.15, 127.77, 126.51, 126.36, 124.46, 123.57, 122.32, 119.30, 91.90, 25.13; IR (thin film) 3098 (m), 3052 (w), 2981 (m), 2926 (w), 1868

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(w), 1792 (w), 1700 (w), 1601 (w), 1506 (w), 1437 (m), 1369 (w), 1326 (w), 1273 (w), 1171 (m), 1126 (m), 1087 (s), 1034 (m), 1020 (m), 974 (w), 939 (w), 901 (w), 862 (w), 851 (m), 830 (m), 822 (m), 753 (m), 698 (w) cm$^{-1}$. Anal. Calcd for $C_{17}H_{16}Cl_2OTi$: C, 57.50; H, 4.54; N, 0.00. Found: C, 57.22; H, 4.44; N, 0.07.

**Bischloro-$\eta^5$-cyclopentadienyl-(1*S*,2*R*,5*S*)-(+)-menthoxy Titanium(IV), 6.** This compound was prepared using the same procedure for the synthesis of **2**. The quantities of reagents used were 0.504 g (2.30 mmol) of $CpTiCl_3$, 0.358 g (2.29 mmol) of (1*S*,2*R*,5*S*)-(+)-menthol, 0.700 mL (0.508 g, 5.02 mmol) of $Et_3N$, and 2 × 25 mL of THF. Yield: 0.707 g (91%) of a yellow solid. Vacuum sublimation of the product at 130 °C yielded 0.305 g (39% recovery) of yellow needle-like crystals: mp = 99−101 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.71 (s, 5H), 4.49 (m, 1H), 2.27 (m, 1H), 2.12 (m, 1H), 1.64 (m, 2H), 1.43 (m, 2H), 1.24 (m, 1H), 0.93 (m, 6H), 0.81 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 118.76, 95.75, 50.50, 44.44, 33.97, 31.78, 25.71, 22.66, 21.97, 20.83, 15.67; IR (thin film THF) 3108 (m), 2958 (s), 2928 (s), 2867 (s), 1855 (w), 1772 (w), 1684 (w), 1457 (m), 1438 (m), 1385 (w), 1368 (m), 1346 (w), 1334 (w), 1267 (w), 1176 (w), 1156 (w), 1095 (m), 1079 (m), 1062 (s), 1048 (s), 1019 (m), 1000 (w), 978 (w), 929 (w), 878 (w), 859 (w), 846 (m), 839 (m), 814 (s), 771 (w), 734 (m), 713 (w), 592 (w) cm$^{-1}$. Anal. Calcd for $C_{15}H_{24}Cl_2OTi$: C, 53.12; H, 7.13; N, 0.00. Found: C, 53.20; H, 7.18; N, 0.11.

**(2-Carbethoxyprop-2-enoxy)bischloro-$\eta^5$-cyclopentadienyl Titanium(IV), 7.** This compound was prepared using the same procedure for the synthesis of **2**. The quantities of reagents used were 3.02 g (13.8 mmol) of $CpTiCl_3$, 1.45 mL (1.60 g, 13.7 mmol) of methyl α-(hydroxymethyl)acrylate [CAUTION: Methyl α-(hydroxymethyl)-acrylate is a powerful skin irritant which has been shown to cause blisters and contact dermatitis upon exposure. Precautions should be taken to prevent exposure to the material and its vapor during handling and storing of the material. Storage in a darkened Schlenk flask at −40 °C is recommended.], 2.00 mL (1.45 g, 14.3 mmol) of $Et_3N$, and 50 + 25 mL of benzene. Yield: 3.39 g (82%) of a yellow solid. The crude product was recrystallized by layering hexanes onto a toluene solution of the compound yielding 1.14 g (34% recovery) of large yellow-orange crystals: mp = 102−104 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 6.75 (s, 5H), 6.34 (m, 1H), 6.00 (m, 1H), 5.34 (s, 2H), 3.78 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) 165.13, 137.03, 126.96, 119.93, 81.60, 52.11; IR (thin film) 3102 (m), 3000 (w), 2953 (w), 2853 (w), 1786 (w), 1715 (s), 1676 (w), 1635 (m), 1438 (s), 1393 (w), 1377 (m), 1304 (s), 1194 (w), 1162 (w), 1040 (vs), 1021 (m), 947 (m), 832 (s), 739 (m) cm$^{-1}$. Anal. Calcd for $C_{10}H_{12}Cl_2O_3Ti$: C, 40.17; H, 4.05; N, 0.00. Found: C, 40.24; H, 4.02; N, 0.00.

**Bischloro-$\eta^5$-cyclopentadienyl(bicyclo[2.2.1]hept-5-enyl)-2-methoxy Titanium(IV), 8.** This compound was prepared using the same procedure for the synthesis of **2**. The quantities of reagents used were 0.842 g (3.84 mmol) of $CpTiCl_3$, 0.465 mL (0.478 g, 3.85 mmol) of *endo*/*exo*-5-norbornene-2-methanol, 0.540 mL (0.392 g, 3.87 mmol) of $Et_3N$, and 2 × 25 mL of benzene. Yield: 1.08 g (92%) of a yellow solid. The crude product was recrystallized by layering hexanes onto a toluene solution of the compound yielding 0.430 g (40% recovery) of yellow crystals: mp = 90−92 °C; $^1H$ NMR (400 MHz, toluene-$d_8$) $\delta$ (ppm) 6.06 (s, 5H), 5.96 (m, 1H), 5.84 (m, 1H), 3.91 (dd, 1H), 3.77 (dd, 1H), 2.97 (s, 1H), 2.57 (s, 1H), 2.18 (m, 1H), 1.54 (m, 1H), 1.39 (m, 1H), 1.01 (m, 1H), 0.22 (m, 1H) [Note: Mostly one isomer, endo or exo, recrystallized. Small signals due to the other isomer were observed in the baseline of the spectrum.]; $^{13}C\{^1H\}$ NMR (100 MHz, toluene-$d_8$) $\delta$ (ppm) 137.58 [next to the solvent signal], 132.53, 118.7, 88.46, 49.61, 44.10, 42.51, 42.03, 28.58; IR (thin film) 3108 (m), 3057 (m), 2967 (s), 2865 (m), 1867 (w), 1773 (w), 1654 (w), 1570 (w), 1449 (m), 1364 (w), 1343 (m), 1256 (w), 1148 (w), 1076 (s), 1017 (m), 930 (w), 824 (s), 723 (m), 692 (m), 646 (m) cm$^{-1}$. Anal. Calcd for $C_{15}H_{24}Cl_2OTi$: C, 53.12; H, 7.13; N, 0.00. Found: C, 53.20; H, 7.18; N, 0.11.

**General Procedure for the Polymerization of *n*-Hexyl Isocyanate. Solution Polymerization.** In a drybox, a volumetric solution of the catalyst, depending upon the monomer-to-initiator ratio, was prepared using the appropriate solvent (for **1** or $TiCl_3OCH_2CF_3(THF)_2$ toluene was necessarily used). To a 25 mL Schlenk tube with a magnetic stir bar, a measured amount (typically 0.100 mL) of this solution was added, and the tube was capped with a rubber septum, taken out of the drybox, and connected to a Schlenk line. *n*-Hexyl isocyanate (1.00 mL, 0.865 g, 6.80 mmol) was added via syringe. The Schlenk tube was fitted with a ground-glass stopper, and the solution was stirred for 24 h.

**Bulk Polymerization.** In a drybox, an appropriate amount of catalyst, depending upon the monomer-to-initiator ratio, was weighed into a 25 mL Schlenk tube with a magnetic stir bar. A drop or two of solvent was added to ensure rapid dissolution of the catalyst into the monomer. The tube was capped with a rubber septum, taken out of the drybox, and connected to a Schlenk line. *n*-Hexyl isocyanate (1.00 mL, 0.865 g, 6.80 mmol) was added via syringe. The Schlenk tube was fitted with a ground-glass stopper, and the solution was stirred for 24 h.

**Polymer Workup.** After the polymerization was complete, the solid orange mass was dissolved in 20 mL of a 5% solution of $CH_3OH$ in THF. This solution was poured into 100 mL of $CH_3OH$, and a white solid precipitated. The polymer was isolated by filtration through a 0.2 $\mu$m nylon filter and washed with $CH_3OH$. Volatile materials were removed under vacuum. The polymer was purified by reprecipitation from THF with $CH_3OH$: total range of yields 74−95%; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ (ppm) 0.82 (br, 3H), 1.22−1.50 (a br and a very br signal, 8H total), 3.60 (very br, 2H); $^{13}C\{^1H\}$ NMR (100.0 MHz, $CDCl_3$) $\delta$ (ppm) 13.92, 22.53, 26.22, 28.42, 31.48, 48.52, 156.77 (lit. 14, 23, 26, 29, 32, 48, 157);[42] IR (thin film) 2953 (s), 2923 (s), 2857 (s), 1700 (s), 1459 (m), 1349 (s), 1265 (s), 1180 (s), 1092 (s), 997 (m), 887 (m), 755 (s) cm$^{-1}$; TGA (onset temperature) 180 °C (100% wt loss) (lit. 180 °C).[43] Anal. Calcd for $C_7H_{13}NO$: C, 66.11; H, 10.30; N, 11.01. Found: C, 66.18; H, 10.71; N, 11.16.

**Endcapping of a *n*-Hexyl Isocyanate Polymerization Initiated by 2 Using Trifluoroacetic Anhydride.** A 25 mL Schlenk flask was charged with 95.8 mg ($3.39 \times 10^{-4}$ mol) of **2** and 0.10 mL of THF. To the slurry of catalyst in THF, 2.00 mL (1.73 g, $1.36 \times 10^{-2}$ mol) of *n*-hexyl isocyanate was added (M/I = 40), and the polymerization was stirred for 48 h. Afterwards, the Schlenk tube was brought into the drybox where 0.864 g of the active polymer was transferred into a flask and taken out of the drybox. This polymer sample was dissolved in 5 mL of a 5% (v/v) $CH_3OH$ in $CH_2Cl_2$ solution and poured into 100 mL of $CH_3OH$. The polymer was isolated by filtration, and solvents were removed under vacuum: yield 0.690 g (80%) of a white solid; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) $\delta$ (ppm) −74.8.

The remaining active polymer was broken apart into pieces and removed from the drybox in the Schlenk tube. Benzene (2.5 mL) was added, and the polymer began dissolving to form an orange solution. Then 1.00 mL (1.49 g, $7.08 \times 10^{-3}$ mol) of trifluoroacetic anhydride was added via syringe, and the solution turned red-orange. Another 2.5 mL of benzene was added to complete the dissolution of the polymer. The solution was stirred for 1 h and then poured into 100 mL of stirring $CH_3OH$. The mixture was filtered, and the polymer was washed with 5 × 10 mL of $CH_3OH$ to ensure removal of any trifluoroacetic acid. Volatile materials were removed under vacuum to yield 0.941 g (90%) of a white solid: $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) $\delta$ (ppm) −70.5, −74.8 [ratio = 1−1.09, 91% endcapped].

Repeat trial using an optimized $^{19}F$ NMR pulse sequence: 69.0 mg (0.244 mmol) of **2**, 0.500 mL (0.433 g, 3.40 mmol) of *n*-hexyl isocyanate (M/I = 14), and 2.00 mL of trifluoroacetic anhydride; yield 0.296 g (68%) of a white solid; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) $\delta$ (ppm) −70.5, −74.8 [ratio = 1.02−1, 100% endcapped].

**Polymerization Kinetic Measurements.** In a drybox, a volumetric solution of the catalyst of interest in toluene was prepared. Several 5 mL volumetric flasks (chosen for the small capacity and for the stable base) were charged with a microstir bar and 0.150 mL of the catalyst solution and then fitted with a rubber septum. The flasks were removed from the drybox. A needle attached to a Schlenk line hose was inserted through the septum, so the flask could be kept under a pressure of argon. The flasks were placed in a water bath thermostatted at 25.0 ± 0.2 °C, and stirring was started. Via syringe, 0.150 mL of *n*-hexyl

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isocyanate was added to the flask, and the time of the polymerization was recorded using a stopwatch. The Schlenk line needle was removed, and the septum and top of the flask were covered with wax film. At timed intervals one of the flasks was opened, and the contents were quantitatively transferred into a 25 mL volumetric flask using HPLC grade $CHCl_3$. The solution was quantitatively diluted to 25.00 mL using HPLC grade $CHCl_3$, and an IR spectrum of the solution was recorded using a 0.1 mm path length NaCl solution cell. The percent transmittance at 2271 $cm^{-1}$ was noted for each of the data points. For polymerizations using catalysts **2**−**4**, depolymerization resulting from the active catalyst end groups was insignificant for up to 1 h after the dilution was performed. For polymerizations using **1**, depolymerization was inhibited by adding 2% (v/v) of THF to the HPLC grade chloroform. The concentrations of monomer in the diluted solutions, and therefore in the polymerizations themselves, were calculated using a Beer's law plot. The concentration of the catalyst in the polymerization was calculated taking into account the dilution factor upon addition of *n*-hexyl isocyanate.

**Depolymerization Kinetic Measurements.** A polymerization of *n*-hexyl isocyanate was conducted using the following quantities of reagents: 18.4 mg ($7.26 \times 10^{-2}$ mmol) of **1**, 0.500 mL of toluene, and 0.440 mL (0.381 g, 2.99 mmol) of *n*-hexyl isocyanate. After completion (3 h), volatile materials were removed from the polymerization under vacuum, yielding 0.336 g (88% yield) of an orange solid. This was dissolved in 1.50 mL of toluene, and the time of depolymerization was kept beginning with the first addition of solvent. The solution was transferred into a 10 mL round-bottom flask, which was then fitted with a rubber septum and taken out of the box. The flask was placed in a water bath thermostatted at 25.0 ± 0.2 °C. Timed aliquots were removed from the depolymerization solution using a syringe and diluted volumetrically using HPLC grade $CHCl_3$. IR spectra of the solutions were recorded using using a 0.1 mm path length NaCl solution cell. The percent transmittance at 2271 $cm^{-1}$ was noted for each of the data points. The concentrations of monomer in the diluted solutions, and therefore in the depolymerization itself, were calculated using a Beer's law plot. The concentration of the catalyst in the polymerization was calculated assuming that all of the catalyst centers from the polymerization were transferred into the depolymerization.

**Thermodynamic Measurements.** In a drybox, a polymerization of *n*-hexyl isocyanate was conducted in a 10 mL Schlenk flask using the following quantities of reagents: 11.6 mg ($4.58 \times 10^{-2}$ mmol) of **1**, 1.00 mL of toluene, and 1.00 mL (0.865 g, 6.80 mmol) of *n*-hexyl isocyanate. After the polymerization had reached equilibrium (3 h), the flask was fitted with a rubber septum, taken out of the drybox, and attached to a Schlenk line. The polymerization was kept under a flow of argon and stirred constantly. The flask was placed in an oil bath equipped with a feedback temperature controller (temperature variation ±0.2 °C) and allowed to reach thermal equilibrium with the oil bath. An aliquot was removed using a syringe and diluted volumetrically using a 2% (v/v) THF/HPLC grade $CHCl_3$ solution. An IR spectrum of the solution was recorded using a 0.1 mm path length NaCl solution cell, and the percent transmittance at 2271 $cm^{-1}$ was noted. The concentration of monomer in the diluted solution, and therefore in the polymerization itself, was calculated using a Beer's law plot. The temperature of the oil bath was increased by an appropriate amount, and the flask was allowed to reach thermal equilibrium with the oil bath. Another aliquot was removed, and the concentration of monomer was determined as described above.

**Observation of the Active Polymer Endgroup Using IR Spectroscopy.** In a drybox, an oligomerization of *n*-hexyl isocyanate was conducted using the following quantities of reagents: 57.6 mg (0.253 mmol) of **3**, 0.050 mL of THF, and 0.600 mL (0.519 g, 4.08 mmol) of *n*-hexyl isocyanate. After completion (24 h), a sample of the oligomerization mixture was placed between NaCl plates, and an IR spectrum was recorded. The plates were then separated, and the oligomerization mixture was exposed to ambient moisture. An IR spectrum was then recorded. Next, 0.174 g of the oligomerization mixture was transferred into a volumetric flask and diluted to 2.00 mL using THF. Some of this solution was placed in a 0.1 mm path length NaCl solution cell, and an IR spectrum was recorded. Another IR spectrum was recorded from which the IR spectrum of a separately prepared background solution of 0.113 g of PHIC in THF was subtracted. The region of interest in all of the spectra was identical. Next, a drop of $CH_3OH$ was added to the oligomerization solution, and an IR spectrum was recorded. Relevant IR stretching frequencies are included within the text.

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