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VERSATILE ORGANOMETALLIC INITIATORS FOR THE LIVING POLYMERIZATION OF ISOCYANATES

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ABSTRACT

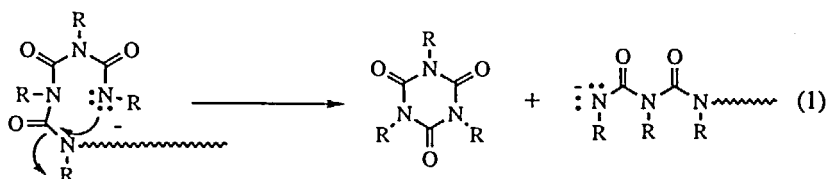
Shashoua and Sweeney first demonstrated that isocyanates could be polymerized via an anionic mechanism to form high molecular weight materials. We have sought to eliminate the problems associated with the anionic procedure by developing transition metal complexes which are capable of catalyzing the living polymerization of isocyanates. Recently, we reported the living polymerization of alkyl isocyanates using $\text{TiCl}_3\text{OCH}_2\text{CF}_3$, **I**. Using **I**, polyisocyanates with controlled molecular weights and narrow polydispersities can be obtained at room temperature. $\eta^5\text{-CpTiCl}_2\text{N}(\text{CH}_3)_2$ (**Cp** = cyclopentadienyl), **III**, is also an excellent catalyst for the polymerization of isocyanates, and in terms of ease of handling and purification and tolerance toward monomer functionality, superior to **I**. In order to prepare triblock copolymers containing amorphous segments sandwiched between two isocyanate segments, we have prepared bimetallic initiators comprised of titanium alkoxides connected by flexible linkers. These linkers may be a small molecule (1,4-dihydroxycyclohexane, **V**) or a polymer (polydimethylsiloxane, PDMS, **VI**). Complexes **V** and **VI** can be used to initiate the living polymerization of isocyanates to yield polymers possessing central cyclohexyl bends

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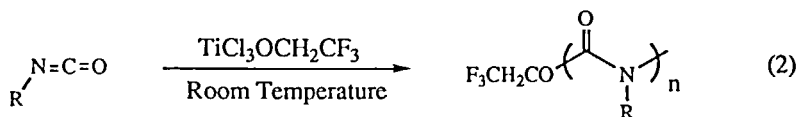
("broken worms") or PDMS segments (triblock copolymers), respectively. Finally, cyclopolymerizations of 1,2-diisocyanates using these organometallic initiators are reported.

INTRODUCTION

By avoiding favored thermodynamic pathways through careful control over kinetics, new reaction profiles can be accessed. Such is the case in the polymerization of isocyanates. Under anionic conditions, backbiting of the amide anion end-group to form the cyclic trimer is moderately slow at low temperature but becomes the predominant reaction above -22°C (Eq. 1) [1].



A few years ago we discovered that even at room temperature this thermodynamic bias could be circumvented by allowing the reaction to propagate through a covalently bound titanium amide complex. This is accomplished by initiating the polymerization with titanium(IV) complexes (Eq. 2) [2].



Through extensive kinetic and molecular weight profile studies, we successfully demonstrated that indeed these titanium(IV)-initiated polymerizations are living.

RESULTS AND DISCUSSION

Since this first report using $\text{TiCl}_3\text{OCH}_2\text{CF}_3$, **I**, we found that cyclopentadienyl titanium alkoxides, amides, and alkyls of the general formula CpTiCl_2X [where $\text{Cp} = \eta^5\text{-cyclopentadienyl}$, and $\text{X} = \text{alkyl} (-\text{CH}_3, \text{II})$, alkoxide ($1^\circ, 2^\circ$, or 3° alkoxides), or amide ($-\text{N}(\text{CH}_3)_2, \text{III}$)] also act to initiate this living polymerization [3]. Substitution of a chloride by the Cp ligand decreases the Lewis acidity of the titanium compound, eliminates redistribution reactions, and lends tolerance to other functional groups. As a result of these factors, the Cp titanium derivatives have become our initiators of choice.

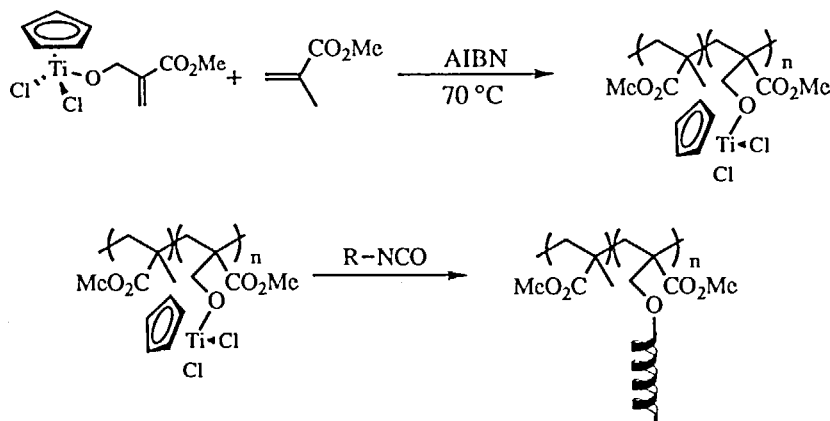
Mechanistic studies have shown that the polymerization is initiated by the specific migratory insertion of an isocyanate monomer into the titanium alkoxide (alkyl, amide) bond. Hence, the alkoxide (alkyl, amide) initially bound to the titanium center becomes the polymer endgroup. Of all of the alkoxides investigated up

to this point, only phenoxide has filed to display this insertion chemistry. Some limitations also exist with the monomers. Primary alkyl isocyanates readily polymerize, but both secondary and tertiary isocyanates do not. Although aromatic isocyanates decompose the Ti(IV) complexes through some undetermined process, benzyl and allylic isocyanates polymerize smoothly.

Once the cyclotrimerization side reaction was eliminated, we discovered that the *n*-hexyl isocyanate, an archetypical primary monomer, has a surprisingly low polymerization ceiling temperature, $T_c = 43.4^\circ\text{C}$. Van Hoff plots reveal $\Delta H^\circ = -8.8$ kcal/mol and $\Delta S^\circ = -28$ eu. In light of this discovery of a low ceiling temperature for primary isocyanates, it is our feeling that the failure of secondary and tertiary isocyanates to polymerize is a ceiling temperature phenomena. Unfortunately, our titanium(IV) complexes are not active enough at temperatures low enough to test this hypothesis.

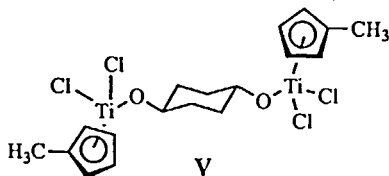
Much of our recent work has been directed at the synthesis and utilization of multifunctional initiators for use in the synthesis of polymers with higher order architectures such as combs, stars, and triblock copolymers. For example, rigid arm combs have been prepared by first synthesizing titanium derivatives with unsaturated alkoxides (IV) and then using these as monomers in free-radical polymerizations [4]. Although poly-IV is completely insoluble, copolymers of IV and methacrylate are soluble in common organic solvents. When these linear organometallic polymers are treated with isocyanate monomer, their pendant titanium alkoxide groups act to initiate the growth of the rigid polyisocyanate arms off of the methacrylate backbone (Scheme 1).

Broken rods can be prepared by initiating the growth of two helical chains off of a common flexible core. We have synthesized a series of bis-titanium complexes, exemplified by V, possessing a flexible, small molecule linker between the two titanium centers [5]. Not all diols are appropriate, with 1,2-diols being particularly problematic. For example, pinicol forms an inseparable mixture of monometallic chelated products and the desired bimetallic compound. In order to eliminate the



SCHEME 1.

possibility of chelation of both alkoxide groups to the same metal center, complexes formed from *trans*-1,4-cyclohexandiol were examined.

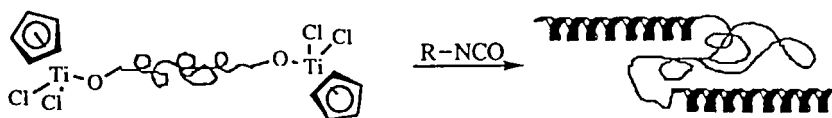


The pure *trans*-1,4-cyclohexandiol was isolated by acetylating a mixture of *cis*- and *trans*-1,4-cyclohexandiol and separating the two isomers through fractional recrystallization. After deprotection, the pure *trans*-1,4-cyclohexandiol was allowed to react with two equivalents of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{TiCl}_3$ in the presence of a base. The solubility and reactivity of the bimetallic catalyst can be controlled by changes to either the linker's structure or the titanium's ligand sphere. Hence, the methylcyclopentadienyl ligand was incorporated into **V** in order to improve the compound's solubility in nonpolar solvents.

Living polymerizations proceed without chain transfer and chain termination steps [6]. Phenomenologically, these undesirable kinetic steps affect the polymerizations differently and require different sets of experiments in order to rule them out: Molecular weight vs conversion plots are used to test for chain transfer reactions while kinetic analyses are used to test for termination steps. Both sets of experiments were performed in order to confirm that complex **V**, like its monometallic, cyclohexyl analogue, $(\text{CH}_3\text{Cp})\text{TiCl}_2\text{OC}_6\text{H}_{11}$, **Ia**, initiates the living polymerization of isocyanates [2]. The plots of molecular weight as a function of monomer to initiator (**Ia** or **V**) ratio are linear, indicating the absence of chain transfer steps. In addition, the kinetic data obtained using **V** to initiate the polymerization of *n*-hexyl isocyanate is consistent with an equilibrium polymerization and is qualitatively and quantitatively identical to the previously obtained data using the monomeric initiators of family **I** [2]. These kinetic studies clearly indicate that no chain termination steps are present. Based on these data, we conclude that **V**, like **I**, catalyzes the living polymerization of isocyanates.

Detailed kinetic analysis of **V** has shown that both its titanium centers are active toward the polymerization of isocyanate monomers [5]. Specifically, competition experiments were performed between **Ia** and **V** at fixed monomer (*n*-hexyl isocyanate) and catalyst (**Ia** or **V**) concentrations. Under these conditions, the [Ti] concentration in the complex **V** initiated runs are set up to be two times the [Ti] concentration in the parallel runs initiated by **Ia**. Under these conditions, the initial rates constants (k_{obs}) measured for these polymerizations were $3.74 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$ and $1.86 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$ for initiators **V** and **Ia**, respectively. The ratio of these rate constants, $k_{\text{V}}/k_{\text{Ia}} = 2.01$, clearly indicates that both titanium centers in **V** are active. Similarly, the fact that the molecular weights of samples collected as a function of time during polymerizations initiated by **V** are approximately twofold larger (vide infra) than the molecular weights of comparable samples collected during parallel **Ia** initiated runs, also indicates that both titanium centers of **V** are active.

By replacing the flexible center block with a telechelic diol, triblock copolymers can be synthesized possessing interesting rod-coil-rod architectures (Scheme 2). In principle, any telechelic diol can be used as a linker. For example, polymeric complex **VI** was synthesized in a manner analogous to **V** using telechelic poly(di-

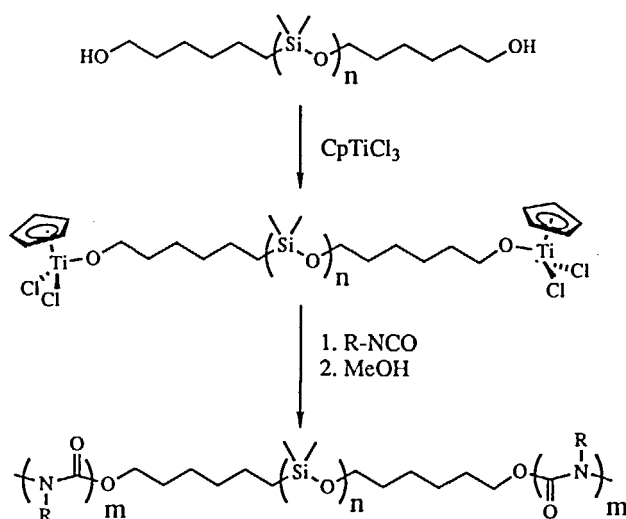


SCHEME 2.

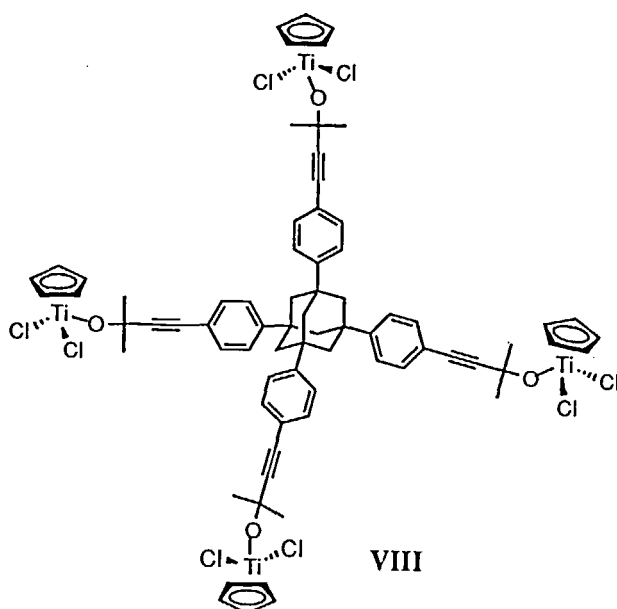
methoxysiloxane) (PDMS) chains ($M_n = 4600$) endcapped with *n*-hexanol groups (Scheme 3) [5].

Telechelic VI polymerizes *n*-hexyl isocyanate in bulk in approximately 4 hours at room temperature to yield (86%) the desired isocyanate-PDMS-isocyanate (poly-VII) triblock copolymer [10]. Evidence for the triblock structure was obtained from ^1H and ^{13}C NMR, molecular weight studies, and solubility comparisons. ^1H and ^{13}C NMR showed poly-VII to contain both poly(*n*-hexyl isocyanate) and PDMS segments. GPC chromatography of poly-VII gave one distinct monomodal peak at $M_n = 11,600$; an increase in M_n from 4600 of the starting poly(*n*-hexyl isocyanate). Lastly, the poly-VII was shown to have markedly different solubility characteristics than poly(*n*-hexyl isocyanate) in that it was soluble in ethyl acetate while poly(*n*-hexyl isocyanate) was not.

We are currently investigating alternative initiators for the synthesis of polymers with more complex structures. For example, we are synthesizing T_d symmetric initiators typified by tetrametallic compound VIII.

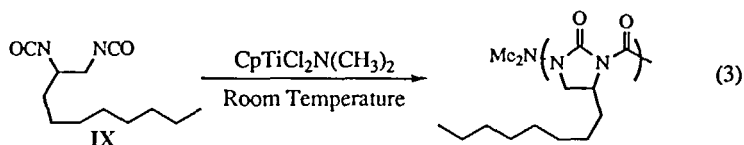


SCHEME 3.



Initiating polymerizations using **VIII** yields stars with rigid polyisocyanate helices radiating from the central core. We predict that these rigid arm stars should behave substantially different than flexible chain stars in rheological studies.

A major limitation with simple poly(alkyl isocyanates) has been their low thermal decomposition temperatures. For example, poly(*n*-hexyl isocyanate) decomposes at ~ 180 – 190°C . The thermal product resulting from this decomposition is the cyclic trimer, which implies a mechanism involving random chain scission followed by rapid intramolecular cyclization [7]. We therefore sought to stabilize these materials by disrupting the facile nature of this cyclization. A means of accomplishing this has been reported in the literature through the cyclopolymerization of 1,2-diisocyanates using anionic initiators [8–10]. Presumably, the resulting fused 5-membered imidazolidone structure effectively blocks the trimerization decomposition pathway and, as a result, these materials show substantially improved thermal behavior. In addition to the thermal stability issue, we were interested in extending the living organotitanium(IV) polymerization methodology to these diisocyanates. As seen in the organotitanium(IV)-catalyzed polymerization of monoisocyanates, the use of a living polymerization provides strict control over the polymer's molecular weight and polydispersity, and allowed for the design and synthesis of well-defined, architecturally interesting macromolecules not obtainable using the equivalent anionic procedure. In order to form soluble polymers, we have investigated the polymerization of 1,2-diisocyanatodecane, **IX**, possessing an octyl side chain. Excellent yields of polymer ($\approx 95\%$) are obtained when initiator **III** is treated with **IX** in THF (Eq. 3).



Poly-IX is soluble in a wide variety of solvents, such as chloroform, THF, benzene, and hexane, which indicates no crosslinking has occurred. The IR spectra of poly-IX showed two carbonyl absorptions at 1778 and 698 cm^{-1} and no absorption at 2270 cm^{-1} , which would have indicated the presence of uncyclized isocyanate groups. These two absorptions have been assigned as the inter-ring carbonyl and intra-ring carbonyl stretching frequencies, respectively [10, 11]. GPC traces of the polymers showed monomodal molecular weight distributions and a range of polydispersities (1.2 to 1.8). A plot of the molecular weight (relative to PS standards) vs the monomer to initiator ratio of the polymerization showed a good linear correlation and a slope (211 $\text{g}\cdot\text{mol}^{-1}$) very close to the molecular weight of the monomer (224 $\text{g}\cdot\text{mol}^{-1}$). The linearity of this plot indicates that chain transfer processes in these polymerizations are insignificant.

Thermal analysis using both DSC and TGA shows that poly-IX decomposes at 276°C, nearly 100°C above the decomposition temperature of poly(*n*-hexyl isocyanate) (180°C), which indicates a substantial kinetic barrier to intramolecular cyclization has been built in poly-IX.

CONCLUSIONS

We have presented a method for the facile polymerization of isocyanates in a living fashion using organotitanium(IV) complexes. By incorporating these initiating centers into more complex molecules, macromolecules with a wide range of structural architectures can be prepared. The possibilities include once-broken rods, diblocks, triblocks, combs, and stars. Finally, the thermal stability of these materials can be greatly enhanced through the cyclopolymerization of 1,2-diisocyanates.

ACKNOWLEDGMENTS

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