Complex Architectures through Living Polymerizations. The Synthesis of "Once-Broken Worms" and Triblock Copolymers Using Bimetallic Initiators

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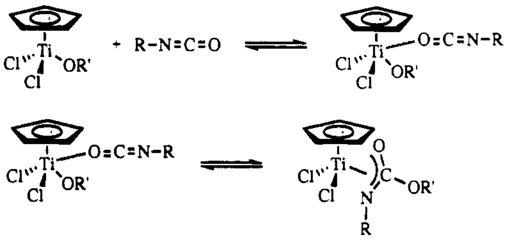
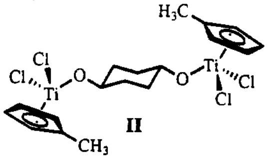
Over the last several years, a major thrust in polymer synthesis has been the development and refinement of organometallic complexes that act to initiate living polymerizations.[1] These new catalysts have permitted the synthesis of polymers having controlled molecular weights, narrow polydispersities, and well-defined end groups. While it has proven feasible to produce block copolymers using some of these living metal mediated polymerization systems,[2] many of these organometallic complexes fail to insert monomers of dissimilar structure. This selective reactivity not only narrows the pool of potential monomers but effectively prevents the sequential formation of many interesting diblock and triblock copolymers. Because of the desirability for block copolymers possessing disparate segments,[3] we have been interested in developing new metal-catalyzed routes into these materials.

Polyisocyanates[4] are a unique class of rigid-chain polymers[5] that adopt 8/3 helical conformations in both solution and the solid state.[6] We have previously reported the use of $CpTiCl_2(OR)$ (Cp = η^5-cyclopentadienide, **I**) (where OR′ can be a 1°, 2°, or 3° alkoxide) as initiators for the living polymerization of alkyl isocyanates at room temperature.[7] Initiation is thought to occur through a migratory insertion of the alkoxide into an isocyanate to form the propagating titanium amidate species (Scheme I). It is important to note that the migrating alkoxide group becomes the polymer chain end.

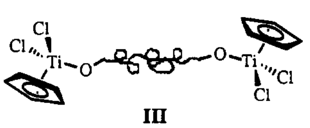
Scheme I



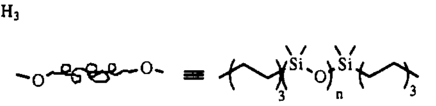
Although isocyanates undergo facile subsequent insertions, the titanium amidate end group is inert toward the insertion of other potential substrates including epoxides, cyclic lactones, acrylates, and methacrylates. We have therefore sought to develop bifunctional initiators that allow the incorporation of flexible segments between rigid polyisocyanate chains.[8] To this end, we would like to report the preparation of bimetallic titanium alkoxides, possessing linker segments that can be either a small molecule (**II**) or a polymer (**III**), and their use in synthesizing either "once-broken worms"[9] or triblock copolymers, respectively.



II

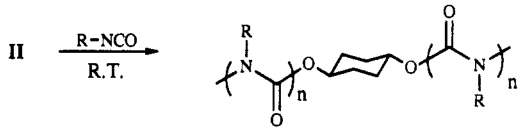


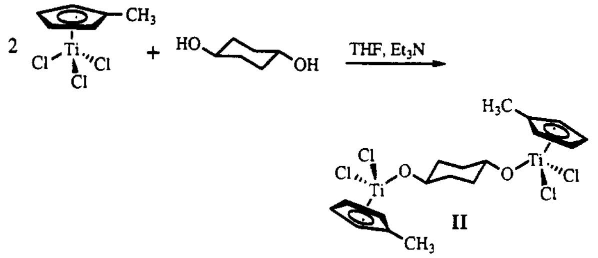
III



In order to test the viability and activity of bimetallic catalysts, we prepared the model compound **II** in 61% yield[10] by the addition of 2 equiv of $(MeCp)TiCl_3$ (MeCp = η^5-methylcyclopentadienide) to 1 equiv of *trans*-1,4-cyclohexanediol[11] (eq 1). Additionally, we prepared both the analogous Cp and Cp* (Cp* = η^5-pentamethylcyclopentadienide) derivatives; however, the Cp compound was too insoluble for polymerization studies, while the Cp* derivative proved to be much less active than the MeCp complex, **II**.

Scheme III





(1)

Compound **II** polymerizes *n*-hexyl isocyanate (HIC) ([HIC] = 3.4 M) in 70–80% yield in approximately 1 day at room temperature (Scheme II). Correcting for ceiling temperature effects ($[HIC]_{eq}$ = 0.6 M at 25 °C), this effectively corresponds to a quantitative conversion.[12] In agreement with our previous studies on simple titanium complexes,[7] a combination of experiments further suggested that the polymerizations of alkyl isocyanates using **II** are living.[13] The plots of molecular weight ($\bar{M}_n$) as a function of either the monomer to initiator (**II**) ratio or the percent monomer consumed are both linear, indicating the absence of chain-transfer steps during polymerizations initiated by **II**.

In order to rule out chain termination steps and to determine whether both titanium centers in **II** are independent chain propagating centers, we studied the rates of polymerization of HIC using both **II** and the analogous monometallic, cyclohexyl complex, (MeCp)-$TiCl_2(OC_6H_{11})$ (84% yield; **IV**).[14] The rate of disappearance of HIC was measured by IR kinetics at 25 °C at identical initial monomer and initiator concentrations for both **II** and **IV**. Under these conditions, the concentration of titanium centers in the reactions initiated using **II** was exactly twice the concentration in the reactions initiated using **IV**. From the slope of a linear plot of $[HIC]_0$–[HIC] versus time, pseudo-zero-order rate constants were determined for the polymerization of HIC by **II** and **IV**. First-order rate constants for **II** and **IV** were then obtained from linear plots of these pseudo-zero-order rate constants versus catalyst concentration (Figure 1). The first-order rate constant for the bisfunctional catalyst (**II**), $k_{II} = 3.6 \times 10^{-3}$ s^{-1}, was found to be exactly twice as large as that for the monofunctional catalyst (**IV**), $k_{IV} = 1.8 \times 10^{-3}$ s^{-1}.

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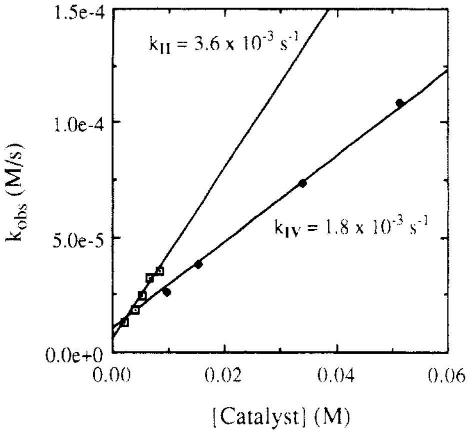


Figure 1. Pseudo-zero-order rate constants, k_{obs}, versus catalyst concentration for the polymerization of HIC by **II** and **IV** ([RNCO] = 3.4 M). An additional point for the plot for catalyst **IV** ([**IV**] = 0.13 M) was deleted for clarity.

Table I. Comparison of $\bar{M}_w$ and $\bar{M}_n$ for the Polymerization of HIC by II and IV[a]

run	$\bar{M}_w$(II)	$\bar{M}_w$(IV)	$\bar{M}_n$(II)	$\bar{M}_n$(IV)
1[b]	7 800	4 600	6 200	3 800
2[b]	10 900	6 700	9 100	5 800
3[b]	30 200	17 200	25 800	15 600
4[c]	58 500	65 700	41 600	45 000

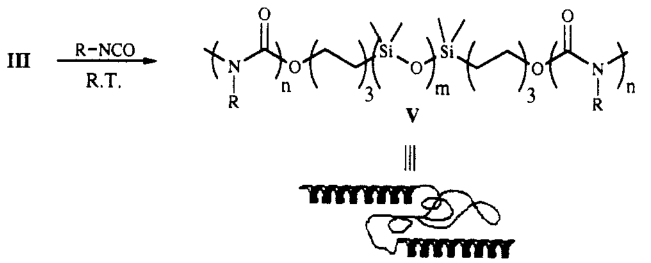
[a] $\bar{M}_w$ and $\bar{M}_n$ were determined by GPC (reported relative to polystyrene standards). $[HIC]_0$ = 3.4 M and [II] = [IV] for all runs. [b] Runs 1-3 were quenched at three different times early in the polymerization, before they had reached equilibrium. [c] Run 4 was quenched once the polymerizations had reached equilibrium.

Hence, we conclude that both titanium centers in **II** are active, and furthermore their activities are neither attenuated nor enhanced by the presence of the proximal titanium center.

Further support for both titanium centers in **II** being active was provided by molecular weight determinations. In competitive polymerizations at fixed initiator ([**II**] = [**IV**], where $[Ti]_{II} = 2[Ti]_{IV}$) and monomer concentrations, the polymerizations initiated by **II** proceed at a rate twice that of those initiated using **IV**. Hence, polymerizations run with **II** under kinetic control (i.e., quenched before obtaining equilibrium) should yield polymers that are twice as large as polymers obtained using **IV** under identical reaction conditions. Under the same conditions but now allowing equilibrium to be obtained, the polymers produced using both initiators should have the same molecular weights. This results from the fact that the partitioning of a fixed amount of monomer between polymer and free monomer is governed by an equilibrium constant, K_{eq} = 1/[monomer], that is independent of both the size and/or number of the chains present. Experimentally, polymer produced by **II** under kinetic control was found to have approximately twice the apparent molecular weight of polymer produced by **IV** under identical conditions (Table I, runs 1-3). Conversely, polymerizations initiated by either **II** or **IV** that were allowed to attain thermodynamic equilibrium yield polymers of approximately the same molecular weight (Table I, run 4).

Rheological studies indicate that polyisocyanates with molecular weights ≤15 000 behave as rodlike chains.[15] Thus, polyisocyanates using **II** containing the flexible cyclohexyl core should behave as once-broken worms. The molecular weights of the polyisocyanates synthesized using **II**, as measured using the GPC,[16] are approximately 10–15% smaller than twice the size of the samples synthesized using **IV** at identical monomer to initiator ratios. We attribute this relative contraction in molecular weight to the differences in the hydrodynamic radii of the rodlike polyisocyanates obtained from **IV** and the once-broken worms obtained using **II**. Support of this hypothesis was obtained from light scattering experiments.[17] Static light scattering (SLS) results for a linear and once-broken polymer, both with GPC molecular weights of 140 000, gave weight-average molecular weights of 30 000 and 52 000, respectively. From dynamic light scattering (DLS) experiments on these same samples, their respective hydrodynamic radii were found to be nearly identical at 6.4 and 7.3 nm. These data support the contention that inclusion of a flexible hinge constitutes a significant change in polymer architecture, where a more massive polymer can be folded into the same hydrodynamic volume.

Scheme III



By modifying the central linker, triblock copolymers can be prepared. Telechelic complex **III**[18] was synthesized in a manner analogous to **II** using telechelic poly(dimethylsiloxane) (PDMS) chains ($\bar{M}_n$ = 2900) endcapped with *n*-hexanol groups[19] (Scheme III).

Polymeric compound **III** polymerizes HIC in bulk in approximately 4 h at room temperature to yield (86%) the desired isocyanate–PDMS–isocyanate triblock copolymer (**V**).[20] 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 **V** to contain both the expected poly(hexyl isocyanate) (PHIC) and PDMS segments. GPC chromatography of **V** gave one distinct monomodal peak at $\bar{M}_n$ = 10 300: an increase in $\bar{M}_n$ from 2900 of the starting PDMS. Last, **V** was shown to have markedly different solubility characteristics than PHIC in that it was soluble in ethyl acetate while PHIC was not.

In summary, we have synthesized bisfunctional catalysts for the living polymerization of isocyanates. These catalysts were shown by kinetic and molecular weight experiments to contain two active titanium centers for chain propagation. Since relatively low molecular weight polyisocyanates act as rigid-chain polymers,[15] the polymers obtained from **II** should be good models for once-broken worms. In addition, telechelic polymeric catalysts were synthesized and used to produce new well-defined triblock copolymers. Future work will concentrate on the properties of these new triblock copolymers, as well as the rheological behavior of the once-broken worms.

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(10) Data for compound II: ^{1}H NMR (CDCl$_3$) δ 6.62 (t, 4H, $J = 2.7$), 6.56 (t, 4H, $J = 2.7$), 5.12 (m, 2H), 2.46 (s, 6H), 2.08 (m, 4H), 1.31 (m, 4H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 135.04, 119.93, 118.37, 89.50, 28.48, 16.26. Anal. Calcd for $C_{18}H_{24}Cl_4O_2Ti_2$: C, 42.40; H, 4.74. Found: C, 42.52; H, 4.81.

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(12) Although these polymerizations are living, they are equilibrium polymerizations run near their ceiling temperatures.[7] This both effects the percent conversion of monomer and tends to broaden the polydispersities of the polymer samples.[13a]

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(14) Data for compound IV: ^{1}H NMR (CDCl$_3$) δ 6.53 (t, 2H, $J = 2.6$), 6.47 (t, 2H, $J = 2.6$), 4.73 (m, 1H), 2.40 (s, 3H), 1.90 (m, 2H), 1.78 (m, 2H), 1.64 (m, 2H), 1.45 (m, 1H), 1.32 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 134.79, 119.71, 117.95, 92.53, 34.83, 25.18, 23.21, 16.31. Anal. Calcd for $C_{12}H_{18}Cl_2OTi$: C, 48.52; H, 6.11. Found: C, 48.44; H, 6.12.

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(16) Measured at 25 °C in chloroform and reported relative to polystyrene standards.

(17) Light scattering measurements performed in THF at 25 °C using a Brookhaven Instrument correlator and goniometer with an argon laser at 488 and 514 nm.

(18) Data for III: ^{1}H NMR (CDCl$_3$) δ 6.08 (s), 0.058 (s); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 119.05, 0.98. Anal. Calcd from GPC: 37.10; H, 8.32. Found: C, 35.84; H, 7.19.

(19) Goldschmidt Chemical Corp.

(20) Data for triblock V: ^{1}H NMR (CDCl$_3$) δ 3.65 (b, 1.02H), 1.59 (b, 1.02H), 1.27 (b, 3.06H), 0.86 (b, 1.53H), 0.057 (s, 1.00H); ^{13}C{^{1}H}NMR (CDCl$_3$) δ 156.76, 48.46, 31.34, 28.35, 26.18, 22.51, 13.90, 0.98. Anal. Calcd from GPC and ^{1}H NMR integration: C, 56.72; H, 9.70; N, 7.80. Found: C, 59.93; H, 9.70; N, 8.72.