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Communications to the Editor

Synthesis of New Rigid Rod Helical Polymers through the Living Polymerization of Carbodiimides Using Titanium(IV) Complexes

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Restricting the conformational degrees of freedom within a polymer's backbone can have the effect of extending the chain and endow the material with a number of interesting properties including high modulus and strength,[1] chirality,[2] and liquid crystallinity.[3] Synthetic routes into rodlike polymers usually involve step growth processes, and consequently, it is often difficult to synthesize these materials with high molecular weights and impossible to obtain narrow polydispersities. In order to access materials with these attributes, we have been interested in developing living,[4] chain growth routes into extended chain polymers. In particular, we have focused on living routes into polyisocyanides[5] with bulky imine substituents that adopt 4/1 helices[6] and alkyl polyisocyanates[7] that adopt 8/3 helical conformations.[8] Although both helical, polyisocyanides and polyisocyanates have widely different conformational and rheological properties because of differences in their respective helix inversion barriers (≥27 kcal/mol[9] vs 3–5 kcal/mol[10]) and persistence lengths (30 Å[7d] vs 600 Å[11]). For various applications, we have been interested in designing systems possessing the persistence lengths of polyisocyanates but with inversion barriers approaching those observed for polyisocyanides. Our conceptual approach to this problem was to replace the carbonyl group in the polyisocyanate backbone with the more sterically demanding imine group of a polyisocyanide (Figure 1).

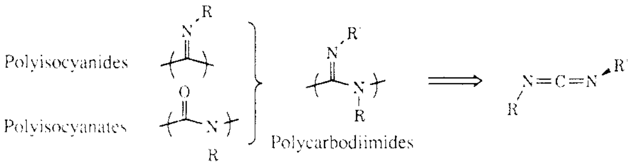


Figure 1. Structural relationship between polyisocyanates, polyisocyanides, and the hybrid polymer derived from the polymerization of carbodiimides.

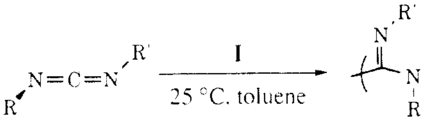
Table 1. Efficacy of Titanium Compounds I–III in the Polymerization of Carbodiimides (R—N=C=N—R′)[a]

carbodiimide	R	R′	I	II or III
1	methyl	*n*-hexyl	yes	yes
2-R/S	methyl	1-phenylethyl	yes	yes
2-R(+)	methyl	(*R*)-(+)-1-phenylethyl	yes	yes
3	methyl	2-phenylethyl	yes	yes
4	methyl	1-phenylpropyl	yes	no
5	methyl	phenyl	yes	yes
6	methyl	*tert*-butyl	no	no
7	ethyl	*n*-hexyl	yes	yes
8	ethyl	1-phenylethyl	yes	no
9	*n*-hexyl	*n*-hexyl	yes	yes
10	phenyl	phenyl	yes	no
11	2-ethyl-*n*-hexyl	2-ethyl-*n*-hexyl	no	no
12	isopropyl	isopropyl	no	no
13	trimethylsilyl	trimethylsilyl	no	

[a] Typical conditions: To a solution of 1.0 mg of either **I**, **II**, or **III** in 1.0 mL of toluene is added quickly 0.25 g of the carbodiimide with stirring (monomer:catalyst ratio ≈ 300:1).

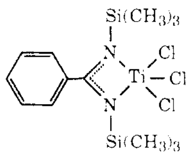
From a retrosynthetic perspective forming this hybrid polymer requires the controlled polymerization of carbodiimides.[12] Low molecular weight polycarbodiimides have been synthesized previously in low yields using ill-defined, nonliving techniques.[13] While polymerizations using thermal techniques and Lewis acids[14] proved to be generally unsuccessful, it has been shown that aliphatic carbodiimides can be oligomerized at low temperatures using *n*-butyllithium as an initiator. Despite varying the monomer to initiator ratios, only low molecular weight polymers were formed. Previously, we have had success in promoting anionic isocyanate polymerizations from nonliving to living status by covalently binding the propagating amide end group to an organotitanium(IV) center.[7b] These covalent titanium amide complexes display a substantially different chemistry than free amide anions, and as a result, detrimental side reactions were eliminated. Because carbodiimides are isoelectronic with isocyanates, we were interested in determining whether a similar approach would tame carbodiimide polymerizations.

Complex **I**, being a structural analog to the suspected lithium amidinate end group in anionic carbodiimide polymerizations, was synthesized[15] and found to be an efficient initiator. For example, nearly quantitative conversion of 500 equiv of di-*n*-hexylcarbodiimide, **9**, is observed in less than 10 s using **I** as an initiator (eq 1).



(1)

I =



Because of the highly exothermic nature of this reaction, initiators with attenuated activities were sought. The cyclopentadienide (Cp) ligand is commonly used to modulate the activity of transition metal complexes.[7a] Attempts to incorporate Cp into **I** or related compounds failed to yield pure compounds. However, we have found that complexes of the type $CpTiCl_2X$ (where X = $N(CH_3)_2$, **II**, and X = OCH_2CH_3, **III**) are polymerization catalysts

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with reduced activity that initiate the *living* polymerization of carbodiimides (*vide infra*).

As shown in Table 1, titanium species **I**–**III** have been found to polymerize a range of monomers that vary in both the steric and electronic environment around the carbodiimide functionality.[16] Inspection of Table 1 allows the following generalizations to be made. Carbodiimides with a tertiary center as a pendent group are not polymerized by these initiators (e.g. carbodiimides **6** and **13**). Carbodiimides with two primary centers are generally polymerized rapidly, but as shown by **11**, β branching on both sides will prevent polymerization. Unlike **II** or **III**, compound **I** will polymerize carbodiimides with aromatic rings surrounding the polymerizable functionality; the slightly larger isopropyl group renders the carbodiimide inert (compare carbodiimide **10** or **12**). Both **I** and **II** (**III**) will polymerize carbodiimides having a methyl and secondary carbon as pendent groups, but **II** (**III**) is slightly more discriminating, as evidenced by the failure of **4** and **8** to polymerize. From these results, it appears that the reactivity is largely determined by the steric demands of the monomer; larger substituents inhibit or prevent polymerization. On consideration of the reactivity displayed between pairs of similar monomers when **II** is used as the polymerization catalyst (e.g., **2**-**R**/**S** or **2**-**R**(+) vs **4**, **3** vs **4**, and **2**-**R**/**S** or **2**-**R**(+) vs **8**), it seems reasonable to suggest that sterics, rather than electronic affects, are also important from the perspective of the catalyst. Replacement of a chloride by a Cp anion, while decreasing the Lewis acidity of the titanium center, also increases the steric encumbrance around the metal center. Predictions as to the success of a polymerization may be based largely on consideration of steric features of both the catalyst and monomer.

We have found that both **I** and **II** display catalytic activity in a variety of solvents including halogenated hydrocarbons (chloroform), hydrocarbons (benzene, toluene, and hexanes), ethers (THF and diethyl ether), and pyridine. Changes in solvent polarity do not appear to affect the polymerization unless the solvent is strongly coordinating. Substantially slower polymerizations were observed in pyridine when compared to other solvents, including THF.

Living polymerizations are chain growth polymerizations free of chain transfer and chain termination reactions.[4] Phenomenologically, these kinetic steps affect polymerizations differently and therefore require different tests to verify their absence. The lack of chain transfer for the polymerization of **2**-**R**(+) by **II** was verified by the successful generation of linear plots of molecular weight versus monomer to initiator ratio (Figure 2). The linearity of this plot indicates that each titanium center initiates only one polymer chain and, most importantly, remains affixed to that polymer chain throughout the entire reaction.

A kinetic study of this polymerization provided additional evidence for its living nature and showed it to be an equilibrium polymerization. While the progress of the reaction was followed, it was observed that monomer was gradually consumed until a final concentration of 1.03 mM at 30.0 °C was reached, independent of the initial concentration of either **II** or **2** or the ratio between those species. Anticipating that polymer formation occurs by the repeated, *and* reversible, coordination/insertion mechanism with a titanium–amidinate acting as the intermediate (eq 2), we proceeded to investigate the equilibrium dependence on temperature. Measurement of the monomer concentration of a polymerization at equilibrium with respect to temperature, and construction of a van't Hoff plot, revealed the thermodynamic parameters governing this reaction to be $\Delta H = -14.0$ (± 0.5) kcal mol^{-1} and $\Delta S = -33$ (± 1) cal mol^{-1} K^{-1} with a ceiling temperature of 157 °C. Similarly, analysis of the kinetic data, with the rate law demanded by a reversible coordination/insertion mechanism, showed that all catalytic centers remain active throughout the course of the reaction for at least 4.9 half-lives and that k_1 has a value of 2.5 (± 0.2) $\times 10^{-2}$ M^{-1} s^{-1}.

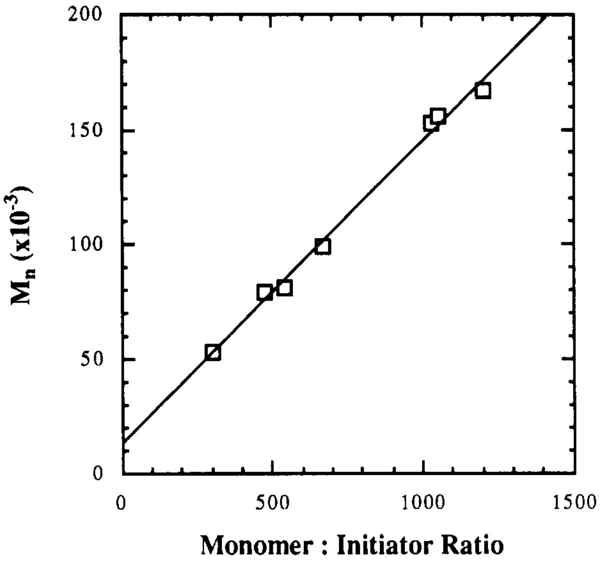
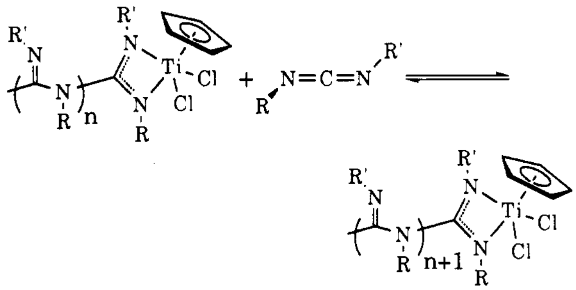


Figure 2. Plot of molecular weight (relative to PS) as a function of the monomer to initiator ratio for the polymerization of **2**-**R**(+) using complex **II**.



(2)

Another indicator of a living polymerization is the ability to synthesize block copolymers. We have found that addition of a second aliquot of **3** to a polymerization solution after 5.0 half-lives have elapsed results in a doubling of the molecular weight (M_w goes from 8.58×10^4 to 1.78×10^5 while M_w/M_n increases slightly from 1.06 to 1.14).

Polycarbodiimides may be isolated, after hydrolysis, precipitation by addition to methanol, and lyophilization from benzene, as a spongy, white solid in 89–95% yields. Analysis of these polymers by gel permeation chromatography (GPC) (relative to monodisperse polystyrene standards) erroneously indicated that the polymer was polydisperse ($M_w/M_n > 15$). However, light scattering measurements (LS) of the effluent polymer demonstrated that very similar molecular weights were eluting over unusually large volumes. This indicates that separation of these polymers is not based strictly on size exclusion, but may involve another phenomenon based on an affinity of these polymers for the GPC column substrate. Analysis by tandem GPC/LS of the polymers that result from a variety of monomer-to-catalyst ratios consistently gave low polydispersities ($M_w/M_n \leq 1.2$).

Now that polycarbodiimides could be synthesized with controlled molecular weights and with narrow molecular weight distributions, systematic investigations into the properties of these macromolecules were initiated. On the basis of evidence obtained from modeling, rheologial, and light scattering studies, these polycarbodiimides appear to vary in conformation from wormlike chains to rigid rods and their degree of extension is highly dependent upon the substituents. From the proportionality relationship, $R_G \ \alpha \ [M_w]^{v}$, the static scaling exponent, v, is highly sensitive to chain conformation.[17] The exponent v will vary from 1/3 for a solid sphere and 1/2 for a Gaussian coil (in a Θ solvent) to 1.0 for a rigid rod. From tandem GPC/light scattering experiments, we found v varies from *ca.* 0.78 for polymers with two primary substituents (i.e., poly-**9**) to 1.0 when a secondary substituent was introduced (i.e., poly-**2-R**(+)). This conformational dependence can be very subtle and even extends to the chirality of the side chain. For example, we investigated the polymerization of both racemic and pure (*R*)-1-(phenylethyl)methylcarbodiimide, **2-R/S** and **2-R**(+), respectively. Both stereoforms readily polymerize using these titanium(IV) complexes. Although these polymers are identical in composition and differ only in the stereoconformation of the side chain, they are distinctly different in both their solution conformations and physical properties. The scaling exponent, v, extracted from the slope of these curves was found to be 0.89 and 1.0 for poly-(**2-R/S**) and poly-(**2-R**(+)), respectively. Hence, poly-(2-(**R/S**) behaves as a wormlike polymer, while poly-(**2-R**(+)) behaves as a true rigid rod. Remarkably, the rodlike character of poly(**2-R**(+)) continues to persist at high molecular weights ($M_w \geq 10^5$). Introducing even small structural irregularities into these polymers in the form of enantiomeric side chains appears to introduce kinks into the polymer backbone and distorts the conformation of these polymers from rods to worms.

Further evidence supporting a well-ordered, extended chain conformation for these polycarbodiimides comes from the unusually large entropy loss associated with their polymerization. The ΔS values of −33 and −38 cal mol^{-1} K^{-1} observed for the polymerization of **2-R**(+) and **9**, respectively, fall outside the typical range of −19 to −29 cal mol^{-1} K^{-1} observed for several polymerizations[18] and, indeed, are substantially larger than the value of −28 cal mol^{-1} K^{-1} we determined for the analogous heteroallene, *n*-hexyl isocyanate;[7b] a polymer known to adopt an extended chain, helical conformation. This exceptionally large value may imply that a considerable amount of order has been imposed on the system that manifests itself as the observed secondary structure.

In conclusion, we have found catalysts which allow for the living polymerization of carbodiimides. This system has proven itself to be quite general, as shown by the variety of conditions, including variations in the monomer and solvents as well as temperature extremes (polymerization have been accomplished from −40 to +107 °C), under which polymerization occurs. Early results from light scattering, rheology, and other physical characterization techniques indicate that the properties these polymers display may be controlled by variation of the pendent groups along the polymer backbone, and this is the subject of current investigation.

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