$$\mathrm{Pt(H)(SiH_3)(PH_3)_2 + {}^{\bullet}CH_3 \rightarrow Pt(H)(CH_3)(PH_3)_2 + {}^{\bullet}SiH_3} \qquad (1)$$

kcal/mol at the MP4(SDQ) level.[18] Therefore, the Si-H bond which is weaker than the C-H bond and the Pt-$SiH_3$ bond which is stronger than the Pt-$CH_3$ bond are considered the main reasons for the larger exothermicity and the smaller activation barrier of the $SiH_4$ oxidative addition than those of the $CH_4$ oxidative addition.

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(18) (a) The p orbital of Si lies higher in energy than that of C, which would favor an interaction between $SiH_3$ and Pt. (b) The relative strength of M-$SiH_3$ and M-$CH_3$ (M = Ti, Zr, or Co) has been theoretically discussed: Ziegler, T.; Tschinke, V.; Versluis, L. *Polyhedron* **1988**, *7*, 1625.

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# "Living" Titanium(IV) Catalyzed Coordination Polymerizations of Isocyanates

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Polyisocyanates[1,2] have received a great deal of attention in recent years due to their chiral helical structure,[3] stiff-chain solution characteristics,[4] liquid crystalline properties,[5] induced optical activities,[6] and molecular weight dependent chain dimensions in solution.[7] Despite this impressive list of unusual properties, the full development of polyisocyanates has been hindered by the lack of efficient synthetic routes.[8] Highly sensitive, low-temperature, anionic isocyanate polymerizations introduced over 30 years ago are not "living", give low yields at low monomer to initiator ratios, and are plagued by a side reaction, namely, back-biting of the active end-group along the polymer chain to form cyclic trimers.[1]

We report that $TiCl_3(OCH_2CF_3)$ (I) and $TiCl_3(OCH_2CF_3)(THF)_2$[9] (II) can *quantitatively* polymerize alkyl isocyanates at room temperature with no detectable formation of cyclic trimer (eq 1). Furthermore, our experimental evidence strongly indicates that these polymerizations are, in fact, "living", and this feature allows for the formation of polyisocyanates of controlled molecular weight and block copolymers.

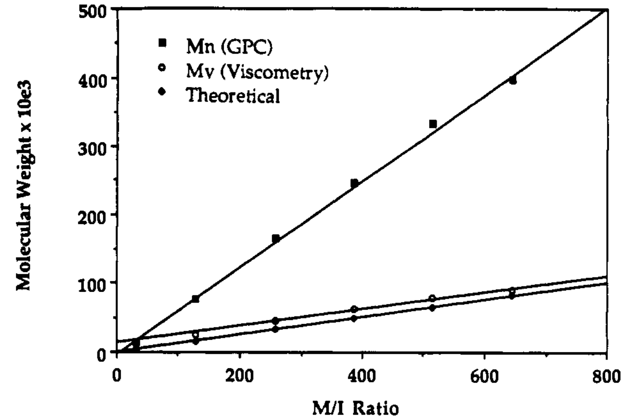


**Figure 1.** Variation in the molecular weight as a function of the monomer to initiator ratio of a typical solution polymerization. $M_n$: determined by GPC relative to polystyrene standards. $M_v$: determined by Ubbelohde type capillary viscometry.

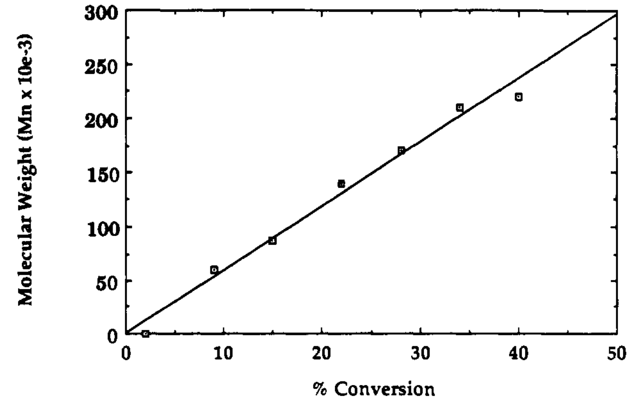
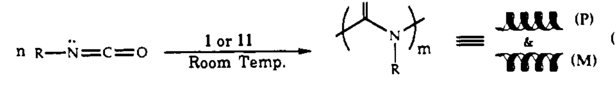


**Figure 2.** Variation in the molecular weight ($M_n$) as a function of the percent conversion of a typical solution polymerization. $M_n$: determined by GPC relative to polystyrene standards. Percent conversion: assessed by correlating the reaction time with kinetic data.



(1)

During initial studies, the yield of polymer systematically varied from 0% to 100% depending upon the initial monomer concentration. Further polymerization-kinetics studies on *n*-hexyl isocyanate revealed that termination processes were not occurring and that these concentration-dependent yields were due to the fact that *polymerizations using I and II are fully reversible between isocyanate polymer and monomer.* This is the first definitive confirmation of ceiling temperature effects in isocyanate polymerizations. Previously, monomer/polymer to trimer transformations were observed.[10] Eromosele and Pepper observed that anionic isocyanate polymerizations displayed ceiling temperature effects; however, it was shown that in this case depolymerization occurred irreversibly to trimer, so it was not a true monomer–polymer equilibrium.[11]

Another unusual feature of polymerizations using I and II is that the polymer can be isolated with the active titanium end-

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**Table I.** GPC Data for Isocyanate Block Copolymerizations

| entry | isocyanate 1 | isocyanate 2 | $M_n$ after 1[a] | $M_n$ after 1 + 2[a] |
|---|---|---|---|---|
| 1[b] | *n*-hexyl | *n*-hexyl | 42 500 | 119 500 |
| 2[c] | *n*-hexyl | *n*-butyl | 46 400 | 155 200 |
| 3[c] | *n*-hexyl | *n*-hexyl | 46 400 | 193 300 |

[a] Determined by GPC relative to polystyrene standards. [b] Without isolation of the polymer plus end-group. [c] With isolation of the polymer plus end-group.

groups intact. Our current proposed mechanism involves coordination and insertion of the isocyanate monomer into a titanium–amidate end-group species.[12] The ability to isolate a polymer with its active end-groups in linear chain-growth polymerizations is quite rare,[13] provides opportunities for studying the polymerization in greater detail, and expands the synthetic usefulness of this polymerization. For example, this "polymeric reagent" can be manipulated in its solid form and redissolved at a later date for use in depolymerization kinetics or for the synthesis of isocyanate–isocyanate block copolymers (vide infra).

The equilibrium behavior of this polymerization ($K_{eq}$ = 2, at ~30 °C) affords a method for measuring the governing solution thermodynamics. Measurement of the variation in the equilibrium constant of the polymerization versus temperature (*n*-hexyl isocyanate, range 20–80 °C) yielded $\Delta H_p = -8.8$ kcal/mol, $\Delta S_p = -28$ cal/(mol·K), and $T_c$ = 43.4 °C[14] ($T_c$ for $[M]_e$ = 1 M; corrections for the variation in the activity of the monomer due to the presence of high polymer were neglected).[15] It is noted that $T_c$ is quite low (between those found for chloral (13 °C) and $\alpha$-methylstyrene (66 °C) polymerizations)[16] and is consistent with the known degree of steric interactions in linear alkyl isocyanate polymers.[17] As expected, cleavage of the active end-group from the polymer chain (methanol wash) results in the expected thermally robust polymer with a decomposition temperature near 200 °C.[10b] In summary, high yields of polymer can be obtained by either (1) decreasing the amount of solvent used (in the limit, a bulk polymerization) or (2) reducing the reaction temperature.

The "living" behavior of this polymerization was demonstrated by several experiments.[18] In a "living" polymerization, $M_n$ should vary as a linear function of the monomer to initiator ratio, and we observe this behavior when using I or II (Figure 1). Also, $M_n$ should vary linearly with the percent conversion of the reaction, which is also observed in these polymerizations (Figure 2).

The titanium end-groups stay active throughout the polymerization until quenched by the addition of protic sources. This is demonstrated by the fact that the polymer chains can be polymerized and depolymerized at will by addition of monomer or solvent, respectively. GPC traces showed no bimodal distributions of molecular weights when fresh monomer was added to a solution of active polymer. Such distributions would indicate that termination or transfer processes had occurred (Table I, entry 1).

The robust nature of the titanium–amidate end-groups can be exploited in the synthesis of block copolymers. Isocyanate–isocyanate block copolymers were prepared by isolating the polymer possessing the titanium end-groups and subsequently redissolving this "active" polymer in the presence of another (or the same) monomer. Several isocyanate blocks were prepared using this method; no bimodal distributions of molecular weights were observed via GPC (Table I, entries 2 and 3).

Finally, the polydispersities of the product polymers range from 1.1 to 1.3. (These values are based on GPC data calibrated relative to the $M_v$ of samples used in this paper and should only be considered approximate.) We are currently studying the kinetics and mechanism of this polymerization and are synthesizing active species analogues.

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**Supplementary Material Available:** Experimental procedures for all polymerizations with characterization techniques and data (3 pages). Ordering information is given on any current masthead page.

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# Cyclization Reactions of a Molybdenum Carbene Complex with 1,3-Nonadien-8-ynes

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Recently we have demonstrated that alkyl methoxy molybdenum carbene complexes will readily produce substituted cyclopropanes when treated with electron-poor olefins.[1] This cyclopropanation process was found to occur under milder conditions and at a faster rate than the analogous process with chromium- and tungsten-derived complexes. We have also demonstrated that, when an alkyne is tethered to the molybdenum carbene complex, vinylcarbene complexes can be generated in situ and trapped by the cyclopropanation of electron-poor olefins to give vinylcyclopropanes in good yield.[2] As part of a project directed toward the development of transition-metal-mediated approaches to polycyclic systems, we report herein the reactivity of 1,3-nonadien-8-ynes with butyl methoxy molybdenum carbene complex **1a**.

On the basis of previous studies by ourselves[1-3] and others,[4] it was anticipated that treatment of dienyne **2**[5] with molybdenum

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