Mono(cyclopentadienyl)titanium Complexes as Initiators for the Living Ring-Opening Polymerization of ϵ-Caprolactone

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Introduction. Ring-opening polymerization of ϵ-caprolactone can be achieved in a living manner using a variety of alkoxo complexes.[1] In particular, aluminum,[2] zinc,[3] and rare-earth alkoxides[4] have attracted much attention as versatile and highly active initiators, allowing the synthesis of block copolymers and end-group-functionalized poly(ϵ-caprolactones). However, most of the highly Lewis acidic alkoxides, usually prepared in situ and therefore not isolated, cannot be considered to be structurally simple.[5] They are presumably aggregated both in solution and in the crystalline state. Most recently transition-metal and lanthanide complexes containing one or two cyclopentadienyl ligands (metallocenes) have emerged as a new class of initiators for homo- and copolymerization of various monomers including functionalized olefins,[6] styrenes,[7] methyl methacrylates,[8] and alkyl isocyanates.[9] They represent structurally well-defined and, on the molecular level, through modification of the cyclopentadienyl ligand, rationally controllable catalyst systems for the polymerization of unsaturated monomers. We report here that crystalline, easily accessible mono(cyclopentadienyl)titanium complexes of the type $Ti(\eta^5\text{-}C_5R_5)Cl_2(OCH_3)$ are capable of polymerizing ϵ-caprolactone with living characteristics and that the substituent pattern of the cyclopentadienyl ligand exhibits a significant effect on the rate of the ring-opening process.

Results and Discussion. Polymerization of ϵ-caprolactone is initiated by $Ti(\eta^5\text{-}C_5H_5)Cl_2(OCH_3)$[10] in a toluene solution or in bulk at 110 °C over a period of several hours. After treating the reaction mixture with methanol, poly(ϵ-caprolactone) can be isolated in good yields as white solids. According to GPC analysis, the molecular weight distribution is narrow and the degree of polymerization is in good agreement with that determined by ^1H NMR spectroscopic end-group analysis (Table I). A sample of molecular weight M_n 30 400 possesses a glass transition temperature of −55 °C and a melting temperature of 67 °C, as obtained from DSC measurements.[11] The linear correlation between the molecular weight M_n determined by GPC and monomer conversion (Figure 1) corroborates that the ring-opening process is indeed living. Inspection of the isolated polymer by GPC and NMR shows that the formation of cyclic oligomers due to "backbiting" as well as products of transesterification is minimal at the early stages of the polymerization. At higher conversions, however, an increase in the molecular weight distribution is observed (entry 6, Table I).

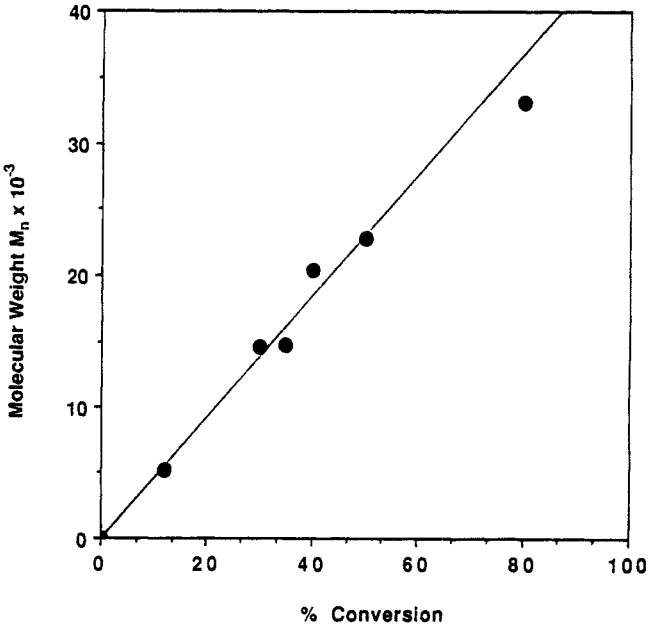

Figure 1. Relationship between the molecular weight M_n and the monomer conversion (%) of poly(ϵ-caprolactone), prepared by $Ti(\eta^5\text{-}C_5H_5)Cl_2(OCH_3)$ in toluene at 100 °C ($[M]_0 = 4.5$ mol/L; $[M]_0/[I]_0 = 305$).

Due to the robustness of the initiator, the ring-opening process can be directly monitored by ^1H NMR spectroscopy, supporting acyl–oxygen cleavage rather than alkyl–oxygen cleavage via the so-called coordinate–anionic mechanism:[1,2] At the initial stage,[12] the titanium alkoxo complex is rapidly converted into a mixture consisting of mono- and oligoinsertion products (Scheme I). It is noteworthy that the spectral features for the product of the first ϵ-caprolactone insertion are clearly distinct from that of the oligomers. Thus, the chemical shifts for the OCH_3 group of the ester group (singlet at 3.43 ppm) and the $TiOCH_2$ group of the "living" end of the growing chain (triplet at 4.12 ppm) are sufficiently distinct from the corresponding values of the oligomeric chain (3.41 and 4.15 ppm, respectively). The monoinsertion product[13] readily reacts with further ϵ-caprolactone present in the reaction mixture. After all the ϵ-caprolactone has been consumed, the growing oligomer with $n \geq 10$ can be isolated as yellow solids after precipitation in ether/hexane. These compounds remain living, i.e., active for further chain growth when redissolved and treated with ϵ-caprolactone, for at least a week under an atmosphere of nitrogen. The ^1H NMR spectrum of a living oligomer with degree of polymerization 27 is depicted in Figure 2. The relative intensity of the proton signals for α-CH_2, OCH_3, $TiOCH_2$, and C_5H_5 is approximately 54:3:2:5. Upon methanolysis the $TiOCH_2$ group is transformed into the hydroxyl end

Table I. Polymerization of ϵ-Caprolactone Using $Ti(\eta^5\text{-}C_5H_5)Cl_2(OCH_3)$ as an Initiator[a]

entry	$[M]_0/[I]_0$	time (h)	% conv (NMR)	DP[b] calcd	DP[c] (NMR)	M_n[c] (NMR)	M_w[d]	M_n[d]	M_w/M_n[d]
1	305	4	12	37	38	4 300	5 400	5 200	1.04
2	305	6	29	89	88	10 100	16 500	14 600	1.13
3	305	8	35	107	120	13 700	17 000	14 800	1.15
4	305	10	40	122	160	18 200	23 700	20 400	1.16
5	305	12	50	153	164	18 700	27 800	22 700	1.22
6	305	18	80	244	270	30 800	50 500	33 800	1.49

[a] Conditions: A toluene solution of the titanium complex was mixed with ϵ-caprolactone and heated to 100 ± 1 °C; ϵ-caprolactone concentration 4.5 mol/L. [b] Theoretical degree of polymerization calculated according to DP = % conv/100$[M]_0/[I]_0$. [c] From ^1H NMR end-group analysis. [d] Determined by GPC analysis (based on PMMA standards).

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Scheme I

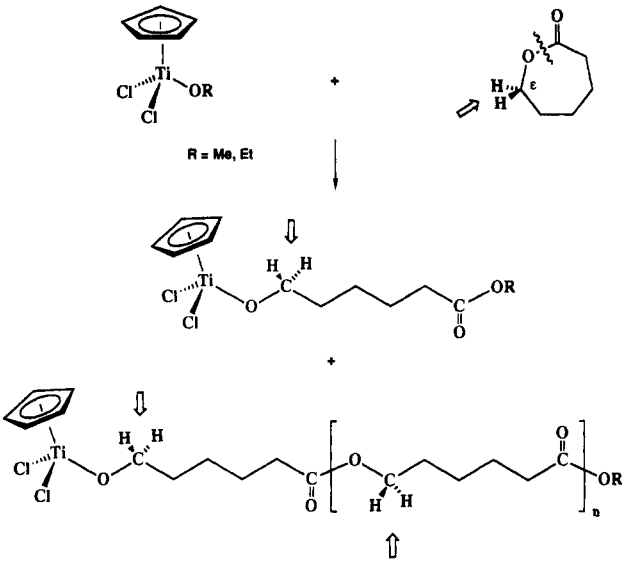

Table II. Relative Rates for the Polymerization of ϵ-Caprolactone Initiated by Various Complexes of the Type $Ti(\eta^5\text{-}C_5R_5)Cl_2(OCH_3)$[a]

R_5 in complex $Ti(\eta^5\text{-}C_5R_5)Cl_2(OCH_3)$	t (min)[b]
H_5	315
$H_4(CMe_3)$	210
$H_2(SiMe_3)_3$-1,2,4	180
$H_3(CMe_3)(SiMe_3)$-1,3	165
$H_2(CMe_3)_2$-4-$(SiMe_3)_2$-1,2	150
$H_4(SiMe_3)$	120
$H_3(SiMe_3)_2$-1,3	96

[a] Condition: 0.051 mmol of the titanium complex was mixed with 1.342 mmol of ϵ-caprolactone in a total solution volume of 0.75 mL of toluene-d_8 in a 5-mm NMR tube. [b] Time required for the reaction to reach 50% conversion at 100 °C.

of the poly(ϵ-caprolactone), as can be monitored by ^1H and ^{13}C NMR spectroscopy.

Although we have so far been unable to perform a satisfactory kinetic analysis, it appears that the propagation step is the fastest. The fact that we are able to observe the first insertion product can be explained by its relative kinetic stability due to an *intra*molecular coordination of the ester terminal via the carbonyl–oxygen atom.

When a series of ring-substituted complexes of the type $Ti(\eta^5\text{-}C_5R_5)Cl_2(OCH_3)$ was examined for the ring-opening reaction, both trimethylsilyl and *tert*-butyl substituents were found to enhance the reactivity of the propagating species. The electron-donating effects of these ring substituents, as observed previously,[14] appear to increase the nucleophilicity of the alkoxo group. However, cyclopentadienyl ligands carrying three substituents were less reactive, indicating that steric effects play a role (Table II).

In conclusion, the present study has demonstrated that well-characterized cyclopentadienyltitanium complexes initiate ring-opening polymerization of ϵ-caprolactone in a living fashion and that, similar to other metallocene-based polymerization initiators, peripheral substituents on the cyclopentadienyl ligand influence the catalysts' performance. Work is underway to expand the ring-opening capability of group 4 mono(cyclopentadienyl) complexes to other heterocyclic substrates and to utilize chiral initiators[15] for stereoselective ring-opening reactions.

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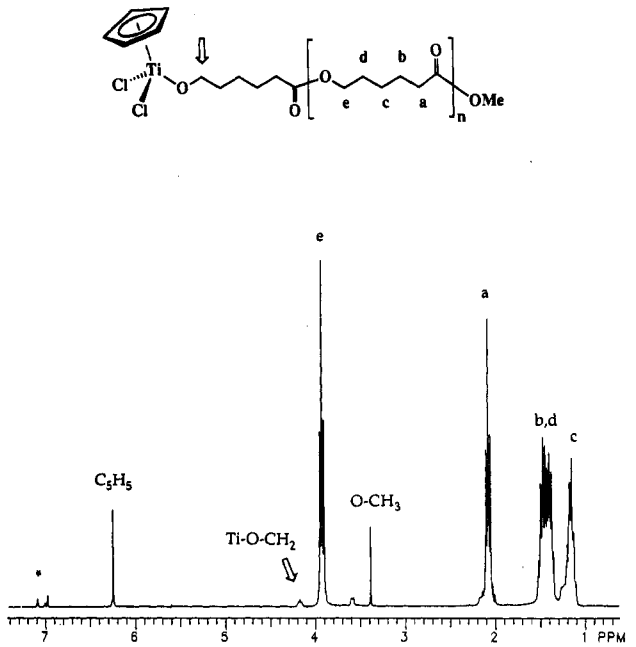

Figure 2. ^1H NMR spectrum of the living poly(ϵ-caprolactone) in toluene-d_8, initiated by $Ti(\eta^5\text{-}C_5H_5)Cl_2(OCH_3)$ at 100 °C ($[M]_0/[I]_0 = 27$).

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(11) Differential scanning calorimetry was performed on a Du Pont DSC 2910 instrument, using 10 mg of sample, a heating rate of 20 °C/min, and a nitrogen purge.
(12) $Ti(\eta^5\text{-}C_5H_5)Cl_2(OMe)$ does not show any sign of adduct formation with ϵ-caprolactone according to NMR, IR, and UV/vis spectroscopy, although coordination of ϵ-caprolactone at the titanium center prior to insertion appears to be probable. See, however, for an example of a stable ϵ-caprolactone

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(13) An authentic sample of $Ti(\eta^5\text{-}C_5H_5)Cl_2(OCH_2CH_2CH_2CH_2CH_2\text{-}CO_2Me)$ was prepared by reacting $Ti(\eta^5\text{-}C_5H_5)Cl_3$ with equimolar amounts of methyl ϵ-hydroxycaproate and triethylamine in diethyl ether. ^1H NMR ($CDCl_3$): δ 6.68 (s, 5 H, C_5H_5), 4.61 (t, J = 4 Hz, 2 H, OCH_2), 3.64 (s, 3 H, OCH_3), 2.30 (t, J = 5 Hz, 2 H, α-CH_2), 1.64 (overlapping multiplets, 4 H, β- and δ-CH_2), 1.42 (m, 2 H, γ-CH_2). ^{13}C NMR ($CDCl_3$): δ 173.91 (CO), 119.23 (C_5H_5), 84.97 (OCH_2), 51.48 (OCH_3), 33.79 (α-CH_2), 32.44 (δ-CH_2), 25.07 (β-CH_2), 24.33 (γ-CH_2). *Cf.* data for $Ti(\eta^5\text{-}C_5H_5)Cl_2(OMe)$. ^1H NMR ($CDCl_3$): δ 6.71 (s, 5 H, C_5H_5), 4.49 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 119.51 (C_5H_5), 72.73 (OCH_3). Reaction of $Ti(\eta^5\text{-}C_5H_5)Cl_2(OMe)$ with *rac*-β-butyrolactone stops at the stage of the monoinsertion to give >90% of $Ti(\eta^5\text{-}C_5H_5)Cl_2(OCHMeCH_2CO_2Me)$: Okuda, J.; Rushkin, I. L., unpublished results.

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