

Figure 2. ^{23}Na DOR spectra of dehydrated Na_{56}Y at various stages of Tl^+ exchange: (a) Na_{56}Y ; (b) $\text{Tl}_8\text{Na}_{48}\text{Y}$; (c) $\text{Tl}_{16}\text{Na}_{40}\text{Y}$; (d) $\text{Tl}_{32}\text{Na}_{24}\text{Y}$; (e) $\text{Tl}_{40}\text{Na}_{16}\text{Y}$; (f) $\text{Tl}_{48}\text{Na}_8\text{Y}$. * indicates spinning side bands. The intensity of the spectra was scaled according to the zeolite Y molar ratio in the sample.

Na^+ cations between accessible sites in the spacious α -cage. However, a more ordered array of "anchored" site II sodium cations is formed upon adsorption of $\text{W}(\text{CO})_6$ into the α -cages of Na_{56}Y , thus restricting the Na^+ to a specific location, with the concomitant emergence of the narrow resonance at around -26 ppm.

^{23}Na DOR spectra of a series of Tl^+ exchanged Na_{56}Y are shown in Figure 2. The intensity of the ^{23}Na peak at -30 ppm decreases as around 15% of the Na^+ cations are exchanged (Figure 2b), and the overall background signal seems to diminish as well. When approximately 30% of the sodium cations are exchanged, the peak at around -30 ppm which is ascribed to the α -cage site II Na^+ is no longer apparent, as shown in Figure 2c. The upfield signal seems to shift to a lower field (Figure 2c), and its intensity decreases somewhat upon progressively loading more Tl^+ cations (Figure 2c-e).

The ^{23}Na DOR spectrum of $\text{Na}_8\text{Tl}_{48}\text{Y}$ shown in Figure 2f displays a diminishingly small remnant of the signal around -40 ppm, while the prominent downfield resonance is split into two signals at -2 and -6 ppm, respectively. The disappearance of the peak at -40 ppm implies that this signal might be associated with site I' Na^+ cations, as in the high Tl^+ loading, these cations may displace Na^+ in the sodalite cages. The Gaussian peak at around -5 ppm is therefore assigned to site I cations. The intense narrow line shape of the DOR resonance from Na^+ cations at site I, which is observed throughout the entire exchange series, is probably due to the essentially octahedral environment experienced by Na^+ at this site, located inside the hexagonal prism between two six-rings. Another factor might be the restricted Na^+ motion anticipated in this site. Thus, although the population of site I Na^+ cations is quite low compared to sites II and I',⁹ the small electric field gradient at the site, as well as the "pinning down" experienced by the Na^+ cations, leads to the relatively narrower peak and higher intensity of the ^{23}Na DOR resonance. The observation

of a well-resolved splitting of the ^{23}Na signal in the spectrum of $\text{Tl}_{48}\text{Na}_8\text{Y}$ indicates the existence of at least two distinct Na^+ site I local symmetries. Since at this stage Tl^+ cations located in the α -cages replace Na^+ in the sodalite cages, this splitting might be related to a nearest-neighbor effect of the Tl^+ cations present in cages adjacent to the hexagonal prisms. The nonobservation of a ^{23}Na signal from site III in our experiments could be due either to the very small Na^+ cation population at this site and/or motion and exchange effects.

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Synthesis of Monodispersed High Molecular Weight Polymers and Isolation of an Organolanthanide(III) Intermediate Coordinated by a Penultimate Poly(MMA) Unit

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Synthesis of high molecular weight polymers ($M_n > 100 \times 10^3$) with extremely narrow polydispersity ($M_w/M_n < 1.05$) remains an important target in polymer chemistry, since such compositionally pure materials must serve as a bench mark for the accurate physical and chemical properties of other polymers. Although various living polymerization systems have been developed, no type of anionic,^{1,2} or cationic polymerization,³ group-transfer polymerization,⁴ or metal carbene initiated polymerization^{5,6} has ever achieved this end. We now report here the first example of high molecular weight poly(methyl methacrylate) with unusually narrow polydispersity (molecular weight distribution), using by the unique catalytic function of $(\text{C}_5\text{R}_5)_2\text{LnR}'$ organolanthanide(III) complexes. The utility of organolanthanides has already been

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Table I. Characterization of Monodispersed Poly(MMA) Synthesized by the Catalytic Action of $[\text{SmH}(\text{C}_5\text{Me}_5)_2]_2^a$

polymerization temp, °C	MMA/initiator charged, mol/mol	$M_n \times 10^3$	M_w/M_n	rr, %	conversion, % (reacn period, h)
40	500	55	1.03	77.3	99 (1)
0	500	58	1.02	82.4	99 (1)
0	1500	215	1.03	82.9	93 (2)
0	3000	563	1.04	82.3	98 (3)
-78	500	82	1.04	93.1	97 (18)
-95	1000	187	1.05	95.3	82 (60)

^a M_n and M_w/M_n were obtained by GPC after calibrating with standard polystyrene whose exact M_w was determined by light-scattering methods.

demonstrated for polymerizations of nonpolar monomers such as ethylene⁷ and conjugated dienes.⁸

As a typical example, the initiation behavior of $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ for polymerizations of methyl methacrylate (MMA) in toluene is summarized in Table I.⁹ Most striking is the very narrow polydispersity, $M_w/M_n = 1.02$ – 1.04 , observed for high molecular weight poly(MMA) of $M_n > 50 \times 10^3$. Secondly, $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ causes the formation of monodispersed polymers in excellent yield at a wide range of polymerization temperatures. Thirdly, high syndiotacticity (rr content, %, r = racemic) exceeding 95% was observed when the polymerization was conducted at -95°C . These results indicate that ideal living polymerization prevails throughout the reaction. In fact, the number-averaged molecular weight (M_n) of resulting polymers increases linearly in proportion to the conversion (polymer yield), while M_w/M_n values (1.03–1.04) remain intact (M_w = weight-averaged molecular weight). The homogeneous polymerization proceeds very rapidly and is complete in 1 h at 0°C when 200 equiv of MMA was charged into the catalytic system. The resulting living polymer bearing a growing poly(MMA) chain of $M_n = 23 \times 10^3$ exhibits an unusually long lifetime, even in the absence of free MMA. Hence, desired living polymerization could reinitiate even after the resulting system is held for 1 hr at 0°C by the sequential addition of 200 equiv of MMA to lead to poly(MMA) of about twice the molecular weight ($M_n = 49 \times 10^3$) with $M_w/M_n = 1.03$.

These observations prompted us to try the isolation of the 1:2 adduct (molar ratio) of $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ with MMA in order to establish the initiation mechanism. As a consequence, the desired adduct **1** could be isolated as air-sensitive orange crystals (mp 132°C), and its structure was determined by single-crystal X-ray analysis (Figure 1). One of the MMA units binds to the metal in an enolate form, and the other, penultimate MMA unit coordinates to the metal at its C=O group. Although similar cyclic intermediates have been proposed for RLi-initiated isotactic polymerization of MMA,¹¹ isolation of the active species had been unsuccessful. In the initiation step, the hydride should attack the CH_2 group of MMA to generate a transient $\text{SmOC}(\text{OCH}_3)=\text{C}(\text{CH}_3)_2$ species, and then the incoming MMA molecule may participate in a 1,4-addition to afford eight-membered-ring intermediate **1**. This prediction is in line with the mode of the 1:2 reaction between $[\text{SmD}(\text{C}_5\text{Me}_5)_2]_2$ and MMA, which gives rise to the formation of $\text{DCMe}(\text{CO}_2\text{Me})\text{CH}_2\text{CMe}(\text{CO}_2\text{Me})\text{CH}_2\text{D}$

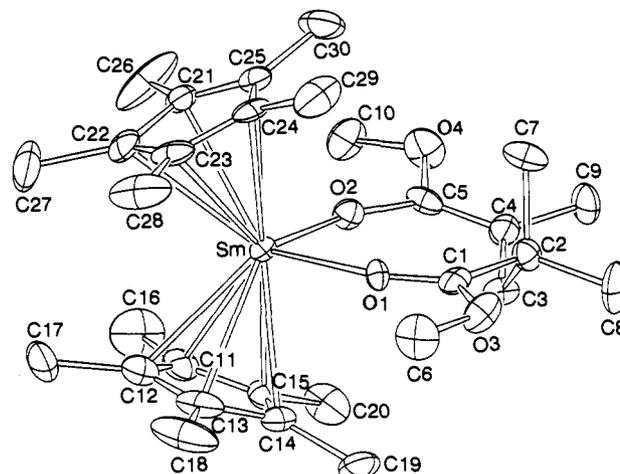


Figure 1. An ORTEP view of the $\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{MMA})_2\text{H}$ intermediate **1**. Selected bond distances (Å): Sm–O(1) = 2.39 (1), Sm–O(2) = 2.188 (9), O(1)–C(1) = 1.23 (2), C(1)–C(2) = 1.53 (2), O(2)–C(5) = 1.31 (2), C(4)–C(5) = 1.39 (2), C(2)–C(3) = 1.61 (2), C(3)–C(4) = 1.52 (2).

quantitatively upon deuterolysis. Since the isolated complex **1** shows excellent catalytic activity and is able to conduct the living polymerization, one can envision adduct **1** as the real active species, i.e., the reaction of 100 equiv of MMA with **1** in toluene at 0°C for 30 min resulted in a quantitative yield of poly(MMA) of $M_n = 12 \times 10^3$ with $M_w/M_n = 1.02$. The mode of organolanthanide catalysis differs greatly from that of typical anionic initiators such as BuLi ¹² and RMgX ,¹³ and only homopolymerization of MMA, not copolymerization, proceeds, even when excess styrene is present in the system. Related complexes such as $\text{YMe}(\text{C}_5\text{Me}_5)_2(\text{OEt})_2$, $[\text{YMe}(\text{C}_5\text{H}_5)_2]_2$, $\text{SmMe}_2\text{AlMe}_2(\text{C}_5\text{Me}_5)_2$, $\text{SmMe}(\text{C}_5\text{Me}_5)_2(\text{THF})$, $\text{YbMe}(\text{C}_5\text{Me}_5)_2(\text{THF})$, and $\text{LuMe}(\text{C}_5\text{Me}_5)_2(\text{THF})$ also exhibit high catalytic activity similarly to $[\text{SmH}(\text{C}_5\text{Me}_5)_2]_2$, and the living syndiotactic polymerization occurred in every case at low temperatures ($< -78^\circ\text{C}$) to afford monodispersed linear poly(MMA) of $M_n = 65$ – 120×10^3 , $M_w/M_n = 1.03$ – 1.05 , and $\text{rr} > 90\%$. The apparent rate of polymerization increases with an increase of ionic radius of the metals ($\text{Sm} > \text{Y} > \text{Yb} > \text{Lu}$) and decreases with an increase of steric bulk of the auxiliary ligands ($\text{C}_5\text{H}_5 > \text{C}_5\text{Me}_5$). On the basis of X-ray structural data and the specific mode of polymerization, we can propose a coordination anionic polymerization mechanism via an eight-membered transition state for the present reaction. Steric control in the polymerization reaction may be ascribed to the intermolecular repulsion between C(7) and C(9) (or the polymer chain) since a completely atactic polymerization proceeds when methyl or ethyl acrylate is used as monomer. The observed unique initiator properties may primarily originate from large ionic radii (1.0–1.1 Å) of rare earth metals as compared with those of Li, Mg, and Al, together with their sufficiently small electronegativity.

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(9) Organolanthanides were used after isolation as single crystals, and all manipulations were performed in Ar using a high-vacuum technique. Monomer was dried over CaH_2 and then molecular sieves 3A, and solvents over Na/K alloy. Polymerization was carried out by the addition of $\text{SmH}(\text{C}_5\text{Me}_5)_2$ to a monomer solution for a fixed time, and then the living end was quenched by the addition of MeOH.

(10) Crystal data for **1**: $\text{C}_{30}\text{H}_{47}\text{O}_4\text{Sm}$, $M = 622.10$, monoclinic with $a = 35.808$ (6) Å, $b = 10.503$ (2) Å, $c = 16.620$ (2) Å, $V = 6143$ (4) Å³, space group C2/c , $Z = 8$, $\mu(\text{Mo K}\alpha) = 7.7 \text{ cm}^{-1}$. The 9427 independent reflections ($2\theta \leq 60^\circ$; $|F_o^2| > 3\sigma |F_o^2|$) were measured on a Rigaku AFC5R diffractometer using ω - 2θ scans. The structures were refined anisotropically to $R = 0.083$ and $R_w = 0.082$.

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Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for **1** (8 pages). Ordering information is given on any current masthead page.

Silaheterocycles. 16.¹ [1,3]-Sigmatropic Migration of an Alkoxy Group: Dichlorosilene to Dimethylsilene Rearrangement

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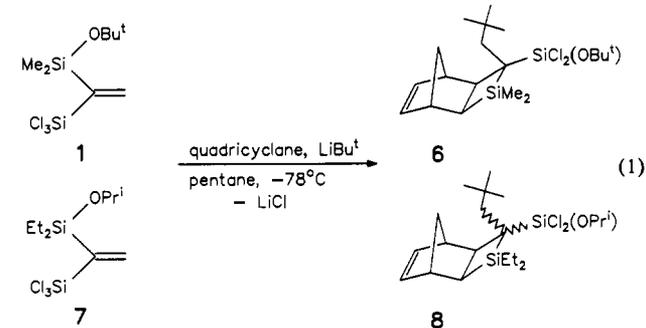
The reactivity of 1,1-dichlorosilenes is different from that of 1,1-diorganosilenes as the studies of 1,1-dichloro-2-neopentylsilene have shown.² Previously we described the cycloaddition behavior of 1,1-dichloro-2-neopentyl-2-(trimethylsilyl)silene.¹ In order to alter the properties of the substituent at the silene's carbon atom we synthesized 1-(*tert*-butoxydimethylsilyl)-1-(trichlorosilyl)ethene (**1**).

The reaction of **1** with *tert*-butyllithium yields silene **2**, which isomerizes to **3**, which can be trapped (Scheme I).

2 cannot be trapped, and even the efficient trap methoxytrimethylsilane only gives **4b**. To discriminate **4b** from **4a**, **5** was synthesized, which shows different NMR resonances for the methoxy groups.

An effective trap for electron-deficient dienophiles is quadricyclane.³ With **3** the exo-[2_σ + 2_σ + 2_π] cycloadduct **6** is formed,⁴ although diorganoneopentylsilenes do not react.^{5,6}

A cross experiment using a 7/1/LitBu/quadricyclane mixture proves intramolecularity (eq 1). Indicative of the rearrangement



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(4) 8-(*tert*-Butoxydichlorosilyl)-7,7-dimethyl-8-neopentyl-7-silatricyclo-[4.2.0.1^{2,5}]non-3-ene (**6**): To **1** and a 3-fold excess of quadricyclane in pentane was added an equimolar amount of LitBu at -78°C . **6** distills as colorless liquid at $110^\circ\text{C}/10^{-2}$ mbar and crystallizes from pentane (mp 115°C): ¹H NMR (CDCl₃) δ 0.31 (s, 3 H, Si(CH₃)₃), 0.52 (s, 3 H, Si(CH₃)₃), 1.00 (s, 9 H, C(CH₃)₃), 1.21 (d, br, 1 H, *J* = 8.60 Hz, C9-*H*-anti), 1.29 (d, br, 1 H, *J* = 8.55 Hz, SiCH), 1.44 (s, 9 H, C(CH₃)₃), 1.55 (d, br, 1 H, *J* = 8.55 Hz, C1-*H*), 1.73, 1.91 (AB, 2 H, *J* = 14.34 Hz, CH₂C(CH₃)₃), 2.41 (d, 1 H, *J* = 8.55 Hz, C9-*H*-syn), 2.76 (s, br, 1 H, C2-*H*), 2.45 (s, br, 1 H, C5-*H*), 5.93 (dd, 1 H, *J* = 5.49, *J* = 3.06 Hz, C4-*H*), 6.43 (dd, 1 H, *J* = 5.49, *J* = 2.44 Hz, C3-*H*); ¹³C NMR (CDCl₃) δ 0.44, 2.57 (Si(CH₃)₃), 23.56 (SiCSi), 29.27 (SiCH), 30.65 (C(CH₃)₃), 31.32, 31.41 (C(CH₃)₃), 40.64 (CH₂C(CH₃)₃), 40.94, 42.24, 44.04 (CH), 45.86 (CH₂), 79.15 (OC(CH₃)₃), 134.79, 138.37 (CH=CH); ²⁹Si NMR (CDCl₃) δ -25.37 (SiCl₂OBu^t), 7.36 (Si(CH₃)₂); *m/e* (EI) *M*⁺ = 404 (0%), 347 (1.03), 256 (1.34), 225 (2.77), 199 (5.74), 57 (100). Anal. Found: C, 56.23; H, 8.39; Cl, 17.52; Si, 14.19. Calcd for C₁₉H₃₄Cl₂OSi₂ (405.56): C, 56.27; H, 8.45; Cl, 17.48; Si, 13.85.

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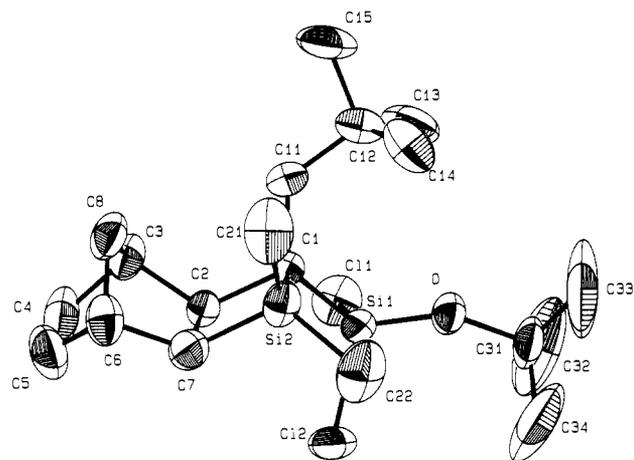
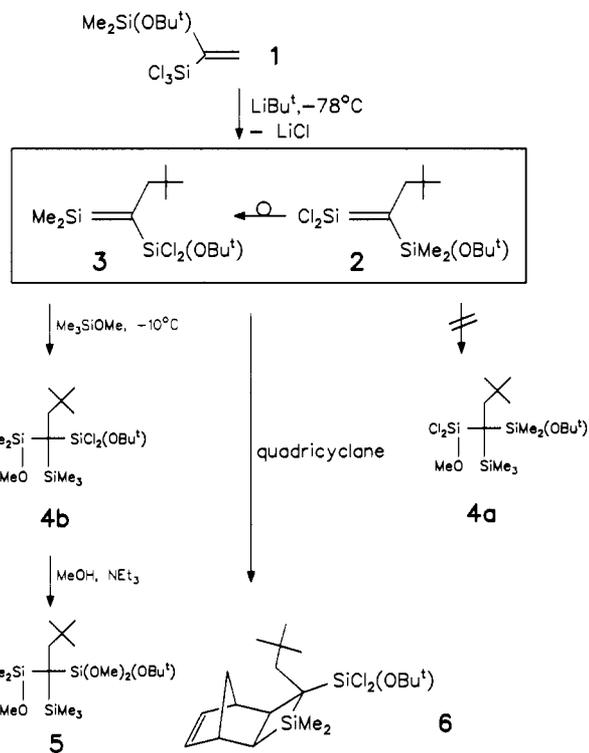
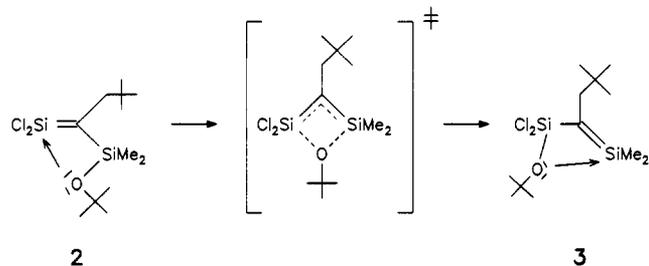


Figure 1. ORTEP representation of **6** (50% probability). Hydrogens are omitted. Bond lengths (Å): Si2-C1 1.92 (2); Si2-C7 1.874 (2); C1-C2 1.609 (3); C2-C7 1.571 (2); Si1-C1 1.851 (1); Si2-C21 1.864 (2); C1-C11 1.567 (3); Si2-C2 2.43 (1); C1-C7 2.47 (3). Bond angles (deg): C1-Si2-C7 81.39 (7); C1-C2-C7 102.2 (1); Si2-C1-C2 86.7 (1); Si2-C7-C2 89.4 (2); Si1-C1-C11 114.6 (2); C1-C11-C12 123.5 (1); O-Si1-C1 113.11 (6).

Scheme I



Scheme II



2 → **3** are the ²⁹Si NMR resonances of **6** at -25.37 and 7.36 ppm with relative intensities 1:5. Resonances in ¹³C and ¹H NMR spectroscopy for dimethylsilyl fragment are inequivalent: it is fixed in the ring system. The exo position of the silacyclobutane ring, which is to be expected from theory⁷ and experiments,³ is proved