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An Easy Synthetic Route to Heteroleptic Samarium Monoalkoxides for Ring-Opening Polymerization Initiators. Molecular Structures of $[(C_5H\textit{i}\text{-}Pr_4)SmI(THF)_2]_2$, $SmI_2O\textit{t}\text{-}Bu(THF)_4$, and $(C_4Me_4P)_2SmO\textit{t}\text{-}Bu(THF)$

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Samarium^{III} monoalkoxides bearing two, one, or no cyclopentadienyl type spectator ligands are easily synthesized by monoelectronic oxidation with *tert*-butylperoxide of the corresponding samarium^{II} precursors. These monoalkoxides are single-site initiators for ring-opening polymerization.

Introduction

Ring-opening polymerization of lactones by lanthanide or yttrium catalysts have attracted considerable attention since the report of McLain concerning the high activity of the clusters $Ln_5(\mu\text{-}O)(OR)_{13}$[1] and of the homoleptic alkoxides $Ln(OR)_3$, isolated or obtained in situ.[2] In these initiators, each −OR function can initiate the growth of a chain, and as a consequence, the complete control of polymerization reactions and the determination of related kinetic parameters are difficult. For a better control and understanding of the polymerization process, the use of lanthanide complexes bearing only one active ligand of general formula SS′LnX, where S and S′ are spectator ligands and X is the functional group allowing the initiation, would be preferable. Moreover, by varying the nature of S and S′ one could estimate a relative importance of stereoelectronic factors governing the polymerization process. Toward this purpose, biscyclopentadienyl hydride or alkyl lanthanide complexes containing only one active site have been looked at,[3] but the difficulty of preparing and handling these complexes has revealed a major drawback for their use. The corresponding biscyclopentadienyl monoalkoxides have been known for some years[4] and are reported as efficient initiators for polymerization of ϵ-caprolactone, δ-valerolactone, and β-propiolactone.[5] Nevertheless, the synthesis of these complexes may be difficult. The general route starting from the chloro derivatives implies the use of an alkali M−OR reagent. However, such a protocol often leads to the formation of anionic “ate” complexes $[Ln](OR)X^-$. It has also been proposed that the pure neutral lanthanide monoalkoxides may be generated in two steps from the corresponding halides: (i) the alkyls, hydrides, or bistrimethylsilylamides are the first synthesized species, and (ii) the alcoholysis of these complexes affords the expected alkoxides[5,6] (an alternative route consists of inserting a ketone into a Ln−H bond[7]). Anyway the synthesis of such species is not simple, and in a peculiar fashion the oxidative route, convenient for samarium or ytterbium derivatives, has not really been useful. We present here the easy and high-yield one-step synthesis of samarium^{III} monoalkoxides from precursors bearing two or one cyclopentadienyl-type ligand, by monoelectronic oxidation of samarium^{II} complexes with organic peroxides.[8]

Results and Discussion

To allow further studies of reactivity, we planned the use as starting materials of a series of samarium complexes containing ligands of different size and electron-donating ability: SmI_2 is commercially available, and the syntheses of bistetramethylphospholyl $(tmp)_2Sm$ (tmp = C_4Me_4P) (**1**) and bistetraisopropylcy-

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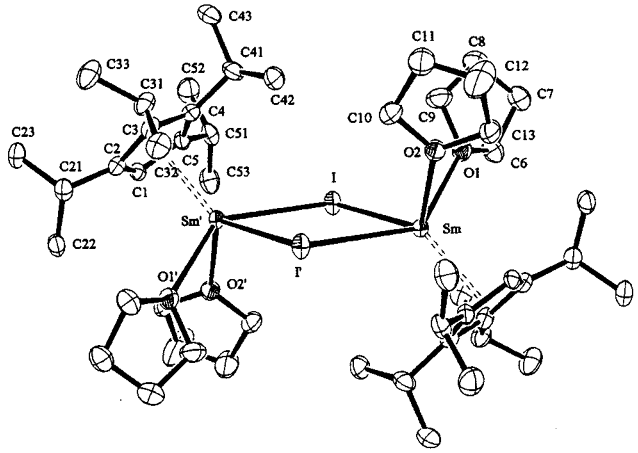

Figure 1. ORTEP drawing of **3** with atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Sm−I′, 3.3020(5); Sm−I, 3.3431(4); Sm−O(1), 2.610(3); Sm−O(2), 2.574(3); Sm−CP, 2.572. Selected angles [deg]: Sm′−I−Sm, 101.228(12); I′−Sm−I, 78.772(12) (CP is the geometric center of C1−C5 carbon atoms of Cp ring).

clopentadienyl $(\mathrm{Cp^{4i}})_2\mathrm{Sm}$ ($\mathrm{Cp^{4i}} = \mathrm{C_5H}i\text{-}\mathrm{Pr_4}$) (**2**) have been previously reported.[9,10] The new iodo monotetraisopropyl cyclopentadienyl $[(\mathrm{Cp^{4i}})\mathrm{Sm}(\mu\text{-I})(\mathrm{THF})_2]_2$ (**3**) was obtained in 79% yield as deep green crystals by comproportionation reaction between stoichiometric amounts of **2** and $\mathrm{SmI_2}$ in THF (eq 1). **3** can also be rapidly prepared from reaction of $\mathrm{SmI_2}$ with 1 equiv of Na $\mathrm{Cp^{4i}}$ in THF (eq 2).

$$(\mathrm{Cp^{4i}})_2\mathrm{Sm} \;+\; \mathrm{SmI_2} \xrightarrow{\text{THF, Rt, 2h}} [(\mathrm{Cp^{4i}})\mathrm{Sm}(\mu\text{-I})(\mathrm{THF})_2]_2 \qquad (1)$$

$$\mathrm{Na}(\mathrm{Cp^{4i}}) \;+\; \mathrm{SmI_2} \xrightarrow{\text{THF, Rt}} 1/2\,[(\mathrm{Cp^{4i}})\mathrm{Sm}(\mu\text{-I})(\mathrm{THF})_2]_2 + \mathrm{NaI} \qquad (2)$$

The dimeric structure of **3** was established by X-ray analysis. The coordination polyhedron of the Sm atom is best regarded as a distorted tetragonal pyramid (Figure 1). It is noteworthy that the coordination number of the samarium atom in **3** is the same as in the previously described $\mathrm{Sm^{II}}$ homologue $[(\mathrm{C_5Me_5})\mathrm{Sm}(\mu\text{-I})(\mathrm{THF})_2]_2$.[11] When the cyclopentadienyl ligand is replaced by a bistrimethylsilyl[12] or a phenoxy[13] group, the samarium atom accepts a third molecule of ether to complete its coordination sphere. The μ-I bridges in **3** are quite symmetric (Sm−I = 3.3431(4) Å, Sm−I′ = 3.3020(5) Å), which reveals strong interactions between the two $\mathrm{Sm^{II}}$ units. Note that with a bulkier pyrazolylborate ligand, the monomeric complexes of divalent samarium or ytterbium were isolated.[14] Hemimetallocenes of the smaller trivalent early lanthanides $\mathrm{Cp^{4i}}$-$\mathrm{Ln(BH_4)_2(THF)}$ (Ln = Nd, Sm) also adopt a monomeric structure.[15]

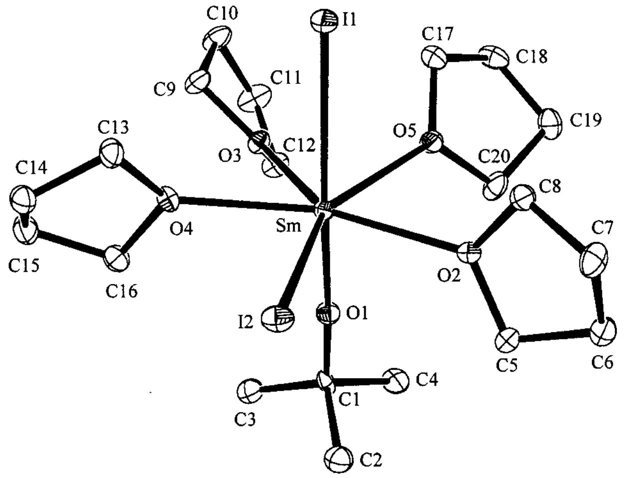

Figure 2. ORTEP drawing of **6** with atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Sm−O(1), 2.084(4); Sm−O(4), 2.469(4); Sm−O(2), 2.474(4); Sm−O(5), 2.496(4); Sm−O(3), 2.522(4); Sm−I(2), 3.1967(7); Sm−I(1), 3.2362(5). Selected angles [deg]: O(1)−Sm−I(1), 173.63(12); I(2)−Sm−I(1), 91.27(2).

The addition at room temperature of 0.5 molar equiv of the peroxide *t*-BuOO*t*-Bu to dark-colored solutions of $(\mathrm{tmp})_2\mathrm{Sm}$ (**1**) and $[(\mathrm{Cp^{4i}})\mathrm{Sm}(\mu\text{-I})(\mathrm{THF})_2]_2$ (**3**) affords the corresponding alkoxides in 65 and 92% yield, respectively (eq 3). In the same conditions, a smooth heating is necessary to perform the oxidation of both $(\mathrm{Cp^{4i}})_2\mathrm{Sm}$ (**2**) and $\mathrm{SmI_2(THF)}_n$. The alkoxide $\mathrm{SmI_2O}t\text{-}\mathrm{Bu(THF)}_n$ had been obtained previously, but not under a crystalline form.[8] This different behavior may be related to the weak affinity of **2** toward ethers, while $\mathrm{SmI_2}$ is obviously more difficult to oxidize for electronic reasons. Wakatsuki et al. described recently a monoelectronic reduction of aromatic ketones involving low-valent lanthanide derivatives, but affording ketyl lanthanide complexes.[16]

$$\mathrm{SS'Sm^{II}(THF)}_n \;+\; 1/2\;{}^t\mathrm{BuOO}{}^t\mathrm{Bu} \longrightarrow \mathrm{SS'Sm^{III}O}{}^t\mathrm{Bu(THF)}_m \qquad (3)$$

4 : S = $\mathrm{Cp^{4i}}$, S′ = I, m = 1
5 : S = S′ = $\mathrm{Cp^{4i}}$, m = 0
6 : S = S′ = I, m = 4
7 : S = S′ = tmp, m = 0

The new complexes $(\mathrm{Cp^{4i}})\mathrm{SmIO}t\text{-}\mathrm{Bu(THF)}$ (**4**) and $(\mathrm{Cp^{4i}})_2\mathrm{SmO}t\text{-}\mathrm{Bu}$ (**5**) were characterized by NMR. The inorganic alkoxide $\mathrm{SmI_2O}t\text{-}\mathrm{Bu(THF)_4}$ (**6**) and the phospholyl complex $(\mathrm{tmp})_2\mathrm{SmO}t\text{-}\mathrm{Bu(THF)}$ (**7**) were isolated as yellow (yield 35%) and orange (yield 65%) crystals, respectively, and identified by X-ray analyses. The coordination polyhedron of the Sm atom in **6** is pentagonal bipyramid with one iodide and alkoxo ligand in axial positions (Figure 2). The axial Sm−I bond of 3.236(1) Å is slightly longer than the equatorial one (3.197(1) Å).

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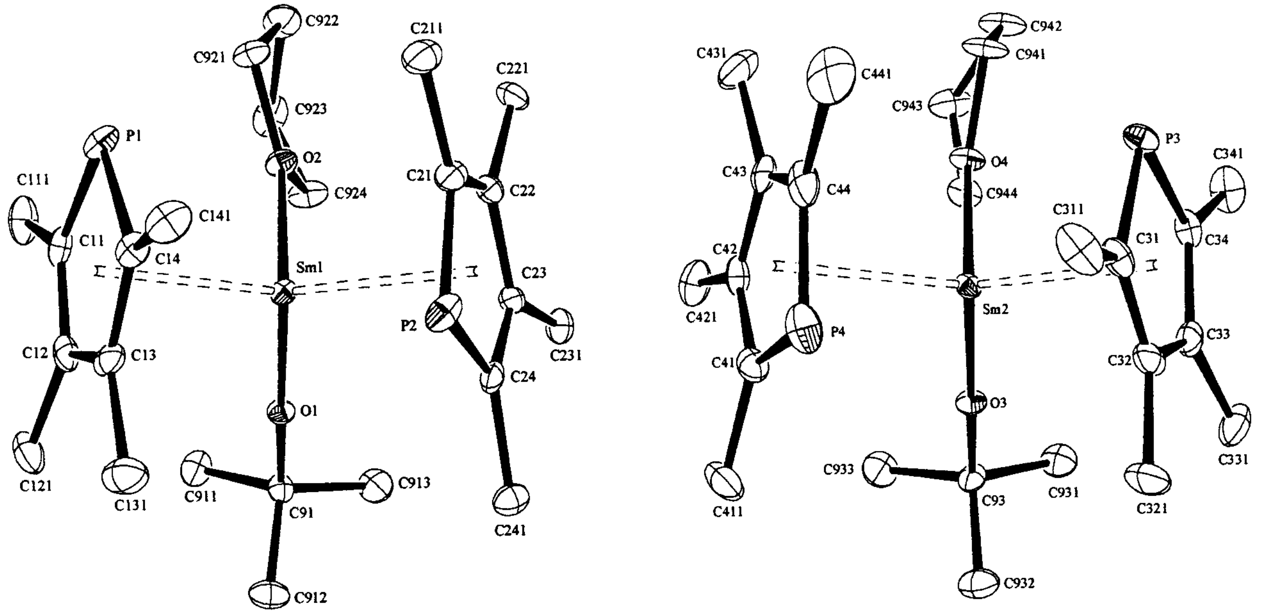


Figure 3. ORTEP drawing of the couple Sm1/Sm2 in **7** with atom-numbering scheme showing the different conformations of THF ligands. Hydrogen atoms are omitted for clarity.

Table 1. Polymerization of ϵ-Caprolactone ([monomer/initiator] = 200; solvent toluene (5 mL); *T* = 20 °C)

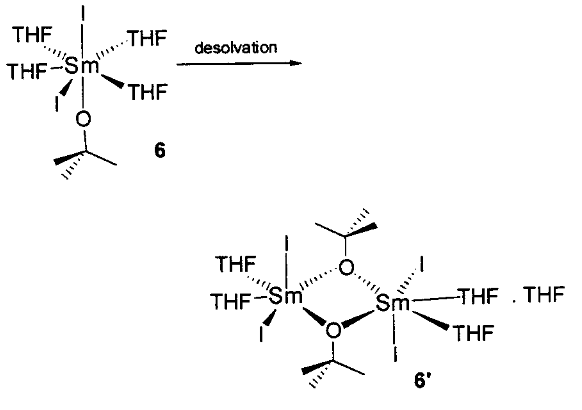
initiator	time (min)	yield (%)	$\bar{M}_n$[a]	DPI[b]
$(Cp^{4i})SmIOt$-Bu(THF) (**4**)	15	95	30 000	1.28
$(Cp^{4i})_2SmOt$-Bu (**5**)	10	80	26 000	1.28
$(tmp)_2SmOt$-Bu(THF) (**7**)	10	70[c]	21 000	1.47
SmI_2Ot-Bu$(THF)_{2.5}$ (**6′**)[d]	30	72	24 000	1.31

[a] SEC measurements vs PS standards using Mark−Houwink corrections. [b] DPI = $\bar{M}_w/\bar{M}_n$. [c] Solvent: 10 mL of toluene. [d] Solvent: pyridine.

In the structure of **7** there are four independent monomeric molecules in the asymmetric unit of the triclinic $P\bar{1}$ space group. The geometries of the molecules Sm1 and Sm4, as well as those of Sm2 and Sm3, are roughly the same, but one observes the different conformations of THF ligands in Sm1/Sm2 and Sm3/Sm4 couples. Such a behavior is shown in Figure 3 for the Sm1/Sm2 pair. The mean Sm−CP (centroid) distance is equal to 2.550 Å with a rather small CP−Sm−CP angle (mean 129.4°). The Sm−O (alkoxo ligand) bond lengths are shorter (mean 2.094(4) Å) than the Sm−O (THF) ones (mean 2.461(4) Å) with the mean value of the O(O*t*-Bu)−Sm−O (THF) angle equal to 90.2(6)°.

In THF or toluene solutions, complexes **4**, **5**, and **7** are active in the ϵ-caprolactone polymerization (Table 1), whereas **6** is surprisingly inactive in the same conditions, but is active when dissolved in pyridine. The molecular weights are close to or somewhat higher than the expected theoretical values calculated from the ϵ-caprolactone/catalyst ratio, and the DPI values are typical of single-site catalyts.

The lack of reactivity of SmI_2Ot-Bu$(THF)^4$ (**6**) in the usual solvents can be related to the observed behavior for this complex: the isolated crystals (obtained from a THF solution) must be kept under THF pressure; otherwise they are very easily desolvated. Within the time necessary to choose suitable crystals for the X-ray structural determination, the transparent brittle crystals turned rapidly opaque. Alternatively, a partially desolvated complex **6′** was isolated as an almost colorless powder after removal of the solvent under vacuum. Both the NMR spectrum, recorded in pyridine-d_5, and the elemental analysis correspond to the formula SmI_2Ot-Bu$(THF)_{2.5}$. Compound **6′** can be active in ϵ-caprolactone polymerization but only after dissolution in pyridine. Obviously, during the desolvation, strong alkoxo bridges are formed (eq 4). The presence of these stable bridges, remaining unchanged in THF, precludes the coordination of ϵ-caprolactone and therefore polymerization. Pyridine, acting as a stronger Lewis base than THF, is able to open the bridges and coordination-polymerization of lactone can occur. Attempts to get a more stable complex by using dimethoxyethane instead of THF were unsuccessful.



(4)

Conclusion

New samarium^{III} monoalkoxides of general formula SS′SmO*t*-Bu can be easily obtained by oxidation of samarium^{II} complexes with *tert*-butyl peroxide. X-ray structure analyses of SmI_2Ot-Bu$(THF)_4$ as well as $(tmp)_2SmOt$-Bu(THF) reveal a monomeric structure in the solid state, while the Sm^{II} hemimetallocene $[(Cp^{4i})Sm(\mu\text{-}I)(THF)_2]_2$, precursor of the heteroleptic $(Cp^{4i})SmIOt$-Bu(THF), adopts a dimeric arrangement.

All the monoalkoxides synthesized act as single-site catalysts for ring-opening polymerization of caprolactone. This is an entry in the area of tailor-made initiators for the ring-opening polymerization. Studies concerning the polymerization ability in the function of the donating character of the ligands will be published in a forthcoming paper.

Experimental Section

All syntheses were performed using a glovebox (JACOMEX) and the standard vacuum line methods. Solvents were dried and deoxygenated over sodium-benzophenone ketyl and distilled at once in the reaction vessel. NMR analyses were conducted in C_6D_6 or TDF at 80 (300 K) or 200 (297 K) MHz, and chemical shifts are referenced vs TMS. Elemental analyses were performed with a CHONS Fisons analyzer. SEC analyses were carried out on a Gynkotek P580A apparatus equipped with two JORDI divinylbenzene mixed B columns and a IOTA2 refractive index detector. Polystyrene standards were used for column calibration, and Mark−Houwink corrections were performed for determination of absolute values of molecular weights. Polymer samples were dissolved in THF (10 mg mL^{-1}), and elutions were performed at 20 °C with THF at flow rate of 1 mL min^{-1}.

Synthesis of $[(Cp^{4i})Sm(\mu\text{-}I)(THF)_2]_2$, 3. $(Cp^{4i})_2Sm$ (**2**, 120 mg, 0.194 mmol) and 79 mg (0.194 mmol) of SmI_2 were loaded in a 50 mL flask which was hooked up to a vacuum line, and 20 mL THF was condensed at −20 °C. The dark green solution was stirred for 2 h at room temperature and filtered through a frit, and the volume of the filtrate was reduced to 5 mL. After layering 5 mL of pentane, the flask was stored for 24 h at room temperature. The dark green crystals were filtered and washed with cold pentane to produce 100 mg of **3** in 79% isolated yield. ^1H NMR (200 MHz, TDF): δ 13.92, 1H (C_5H); 9.01, 6H (CH_3); 8.17, 6H (CH_3); 3.86, 1H ($CH(CH_3)_2$); 2.25, 6H (CH_3); 0.20, 1H ($CH(CH_3)_2$); −3.25, 6H (CH_3). Anal. Calcd for $C_{25}H_{45}O_2ISm$: C, 45.83; H, 6.92. Found: C, 45.76; H, 6.96.

Synthesis of $(Cp^{4i})SmIOt\text{-}Bu(THF)$, 4. 3 (98 mg, 0.15 mmol) and 11 mg (0.075 mmol) of *t*-BuOO*t*-Bu were loaded in a 20 mL flask, and 5 mL of toluene was condensed at −20 °C. The solution was stirred for 10 min at room temperature, and toluene was removed to give 91 mg (92% yield) of a yellow powder. ^1H NMR (200 MHz, C_6D_6): δ 12.29, 1H (C_5H); 4.24, 9H (*t*-Bu); 3.58, 1H ($CH(CH_3)_2$); 2.99, 4H (THF); 2.08, 6H (CH_3); 1.24, 6H (CH_3); 1.05, 4H (THF); 0.74, 1H ($CH(CH_3)_2$); −0.64, 6H (CH_3); −1.40, 6H (CH_3).

Synthesis of $(Cp^{4i})_2SmOt\text{-}Bu$, 5. $(Cp^{4i})_2Sm$ (10 mg, 1.61 × 10^{-5} mol) and 1.71 mg (8.03 × 10^{-6} mol) of *t*-BuOO*t*-Bu were loaded in a NMR tube, and 0.5 mL of C_6D_6 was condensed. After 20 min at 70 °C, the solution became yellow. ^1H NMR (200 MHz, C_6D_6): δ 18.76, 2H (C_5H); 7.90, 2H ($CH(CH_3)_2$); 5.22, 12H (CH_3); 1.98, 12H (CH_3); 0.83, 12H (CH_3); 0.40, 2H ($CH(CH_3)_2$); −1.91, 12H (CH_3); −5.71, 9H (*t*-Bu).

Synthesis of $SmI_2Ot\text{-}Bu(THF)_4$, 6. SmI_2 (372.5 mg, 0.92 mmol) was loaded in a 50 mL flask and stirred with 20 mL of THF. After SmI_2 was dissolved, the blue mixture was poured onto 67.4 mg (0.46 mmol) of *t*-BuOO*t*-Bu. The solution was heated at 50 °C for 20 min and turned yellow. After filtration, concentration at 5 mL, and storage for 2 days at −30 °C, THF was discarded and the brittle yellow crystals of **6** (250 mg, yield 35%) were stored with a small amount of the mother liquor. From a sample of **6**, complete removal of the solvent afforded a very pale yellow powder **6′**. ^1H NMR (pyridine-d_5, 200 MHz): δ 3.66, 10H (THF); 3.09, 9H (CH_3); 1.63, 10H (THF). Anal. Calcd for $C_{14}H_{29}O_{3.5}I_2Sm$: C, 25.57; H, 4.45. Found: C, 25.36; H, 4.64.

Synthesis of $(tmp)_2SmOt\text{-}Bu(THF)$, 7. $(tmp)_2Sm$ (380 mg, 0.886 mmol) and 64.8 mg (0.443 mmol) of *t*-BuOO*t*-Bu were loaded in a 50 mL flask, and 20 mL of toluene and then 5 mL of THF were condensed at −20 °C. The solution was stirred for 10 min at room temperature and was stored for one night at 0 °C after concentration at 10 mL. The crystals were collected and redissolved in 20 mL of pentane. The solution was concentrated at 5 mL and stored for 3 days at −35 °C. The orange crystals were collected on a frit and dried under vacuum: 290 mg, 65% yield. ^1H NMR (C_6D_6, 200 MHz): δ 3.98, 9H (*t*-Bu); 3.68, 6H (CH_3); 2.05, 6H (CH_3); 0.9, 12H (CH_3); −1.91, 4H (THF); −2.29, 4H (THF). Anal. Calcd for $C_{24}H_{41}O_2P_2Sm$: C, 50.23; H, 7.20. Found: C, 50.08; H, 7.32.

Polymerization Experiments. Typical experiments were carried out in THF or toluene at 20 °C by adding 2.5 mL of a 5 × 10^{-3} M solution of ϵ-caprolactone to 2.5 mL of a 10^{-5} M solution of the initiator. Typical monomer-to-initiator ratio is about 200. The polymerization is stopped when the medium becomes so viscous that stirring is not possible. The flask is opened, and an adequate amount of solvent is added to dissolve the gel. The polymer is precipitated into ethanol, isolated, and dried under reduced pressure.

Crystal Structure Determination. All data were collected on a Nonius Kappa CCD diffractometer at 110.0(2) K using Mo Kα radiation (λ = 0.71073 Å) for all the complexes. Full details are given in the Supporting Information.

Crystal Data for $C_{58}H_{106}O_6I_2Sm_2$ (3): (including two molecules of THF per unit); M = 1453.93; monoclinic; space group $C2/c$; a = 25.717(2) Å, b = 18.477(2) Å, c = 16.380(2) Å, β = 127.22(1)°, V = 6197.9(11) Å^3; Z = 4; D = 1.558 g cm^{-3} ; μ = 2.916 mm^{-1} ; $F(000)$ = 2928; crystal dimensions 0.15 × 0.08 × 0.06 mm; 7651 reflections collected, 6001 of which with $I > 2\sigma(I)$; goodness of fit on F^2 1.015; R1 = 0.0345 ($I > 2\sigma(I)$; wR2 = 0.0999 (all data); maximum/minimum residual density 0.785/−1.112 e Å^{-3}.

Crystal Data for $C_{20}H_{41}O_5I_2Sm$ (6): M = 765.68; monoclinic; space group $P2_1/n$; a = 12.2630(10) Å, b = 12.908(2) Å, c = 18.197(3) Å, β = 73.430(10)°, V = 2760.8(7) Å^3; Z = 4; D = 1.842 g cm^{-3} ; μ = 4.387 mm^{-1}; $F(000)$ = 1476; crystal dimensions 0.15 × 0.08 × 0.08 mm; 10 483 reflections collected, 5515 of which with $I > 2\sigma(I)$; goodness of fit on F^2 1.150; R1 = 0.0399 ($I > 2\sigma(I)$); wR2 = 0.1052 (all data); maximum/minimum residual density 1.300/−1.831 e A^{-3}.

Crystal Data for $C_{24}H_{37}O_2P_2Sm$ (7): M = 569.32; triclinic; space group $P\bar{1}$; a = 17.5521(5) Å, b = 18.4566(5) Å, c = 18.6919(5) Å, α = 100.558(1)°, β = 116.375(1)°, γ = 91.048(2)°, V = 5298.8(3) Å^3; Z = 8; D = 1.429 g cm^{-3} ; μ = 2.353 mm^{-1}; $F(000)$ = 2312; crystal dimensions 0.4 × 0.2 × 0.1 mm; 23 400 reflections collected, 21 864 of which with $I > 2\sigma(I)$; goodness of fit on F^2 1.020; R1 = 0.0447 ($I > 2\sigma(I)$); wR2 = 0.1106 (all data); maximum/minimum residual density 1.435/−1.603 e Å^{-3}.

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Supporting Information Available: Crystal data, intensity measurement, structure solution and refinement, tables of positional and thermal parameters, and bond distances and angles (compounds **3**, **6**, and **7**). This material is available free of charge via the Internet at http://pubs.acs.org.

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