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Influence of rare earth compounds on the anionic ring-opening polymerization of cyclosiloxanes

G. Richard[1], A.-F. Mingotaud[1], D. Cardinaud[2], A. Soum[1,*]

[1] Laboratoire de Chimie des Polymères Organiques, UMR 5629, E.N.S.C.P.B.,
Avenue Pey Berland-BP 108, F-33402 Talence Cédex, France
[2] Rhône-Poulenc Silicones, C.R.I.T. Carrières, F-69192 Saint Fons Cédex, France

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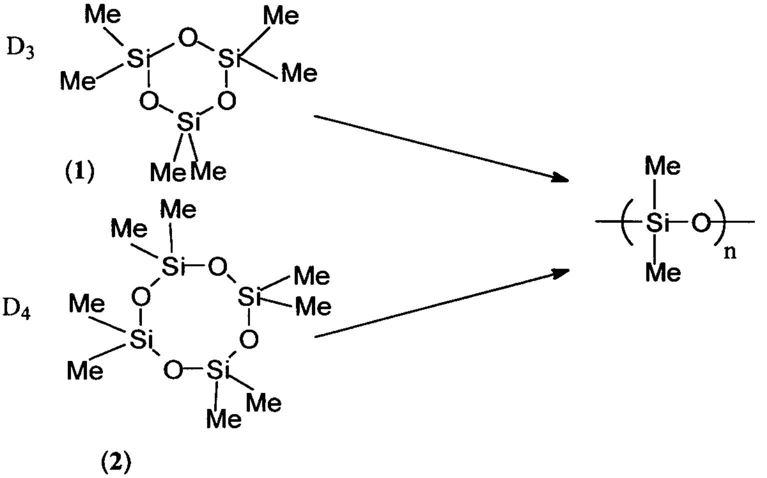
Summary

The influence of rare earth compounds on the polymerization of cyclosiloxanes has been studied for hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4). In both cases, it has been shown that rare earth compounds alone do not lead to well defined polymers : yields are never quantitative and the formation of cyclic side-products is always observed. The influence of these compounds has also been studied in the anionic polymerization of the same cyclosiloxanes initiated by organolithium reagents or fluorides. In the case of D_3, it has been shown that back-biting reactions can be slowed down in the presence of rare earth compounds whereas for D_4, both polymerization and back-biting reactions get slower.

Introduction

Cyclosiloxanes are certainly some of the most important monomers since they lead (through ring-opening polymerization) to polysiloxanes (i.e. silicones) (Eq. 1). Their polymerization has been described in many reviews (1-3) and two of these cyclic monomers have been more particularly studied: hexamethylcyclotrisiloxane (D_3) (**1**) which is the most reactive (due to its strained ring) and octamethylcyclotetrasiloxane (D_4) (**2**) which is the most easily obtained through the hydrolysis of dimethyldichlorosilane.



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* Corresponding author

The major problem of the anionic ring-opening polymerization of these cyclosiloxanes is the occurrence of side-reactions (particularly back-biting and redistribution reactions) simultaneously to the propagation step (3,4). This leads to the formation of cyclic oligomers beside the polymer and to a change of the polymer functionality along with a broadening of the molecular weight distribution. For instance, in the polymerization of D_4 (initiated, in bulk, by potassium hydroxide at high temperature), the highest polymer yield obtained is around 85%. In the case of the polymerization of D_3, the synthesis of the polymer is well controlled for conversions which remain below 95% ; if the conversion reaches 100%, then side-reactions occur leading to cycle formation and broadening of the molecular weight distribution.

Therefore, the control of the ring-opening polymerization of such monomers (i.e. foreseeable molecular weight, narrow molecular weight distribution) is an important industrial challenge. This prompted us to undertake this work in order to evaluate the efficiency of various new initiators (or various initiating systems) in decreasing the yield of side-products without decreasing that of polysiloxane.

Experimental

Materials: D_3 was purchased from Aldrich whereas D_4 was obtained from Rhône-Poulenc. They were dried over calcium hydride, at 80°C for D_3 and at ambient temperature for D_4; they were then vacuum trap-to-trap distilled before use. Toluene and THF were distilled from sodium/benzophenone and stored on sodium. DMF was distilled from NaOH and stored on molecular sieves 3Å. Rare earth compounds were obtained from Strem Chemical and were used, without further purification, in a glove box under inert atmosphere.

Polymerizations: Polymerizations were carried out under vacuum, in a reactor equipped with Rotaflo® taps. In a typical experiment, the lanthanide and the initiator were introduced in the lower part of the reactor and dissolved in the solvent. The monomer was introduced, in solution, in the upper part of the reactor. The apparatus was regulated at the temperature of the experiment and the polymerization was started by adding the monomer on the solution of initiator and additive. Samples (for GC and SEC analyses) were withdrawn at various reaction times by pouring part of the solution into a tube where polymerization was quenched by acetic acid. The polymers were recovered by precipitation in methanol and dried under vacuum.

Characterizations: Gas chromatography (GC) measurements were performed on a DELSI DI 200 (thermal conductibility detection) equipped with a BP1 Macrobore (12,5mx0,53mm) capillary column and a Varian integration system. The temperature program was 10°C/min from 50 °C to 240 °C. The internal standard method and the experimental response factors were used for the determination of the various product concentrations.

Size-exclusion chromatography (SEC) measurements were carried out in toluene by using a Varian liquid chromatograph equipped with four TSK columns (G4000HXL, G3000HXL, G2000HXL, G1000HXL) and refractive index detection. Molecular weights were calculated using polysiloxane standard calibration curve.

Results and discussion

In the first part of this work we evaluated the efficiency of rare earth derivatives as initiators of the ring-opening polymerization of cyclosiloxanes D_3 and D_4. The results presented in Tab.1 show that, with these initiators, the polymerization yields are never quantitative even for long time of reaction and that there is always formation of a significant amount of cyclic side-products. Furthermore, comparing the values of $\overline{M}_{n\,th}$ and $\overline{M}_{n\,exp}$ (calculated including both cyclic and linear oligomers), several observations can be done. Initiation by $Y(OiPr)_3$ at 120°C leads to a good agreement for D_3 and to a disagreement for D_4 ($\overline{M}_{n\,th}$ / $\overline{M}_{n\,exp}$ range between 1,2 and 1,8). This shows that only one alkoxyde group has initiated the polymerization of D_3, and between one and two for D_4. The lowering of the reaction temperature drastically decreases the conversion in polymer. In that case, the low efficiency observed could be attributed to the low solubility of the rare-earth derivative in the solvent. The same reason can be proposed to explain the results obtained with $La(OTf)_3$.

Tab.1.Polymerizations of D_3 (**1**) and D_4 (**2**) initiated by rare earth compounds, in toluene, at 120 °C

M	Initiators	$[M]_0$ mol/L	10^2 $[I]_0$ mol/L	t(h) [a]	%Pol. [b]	%Cycl. [c]	%M [d]	$\overline{M}_{n\,exp}$ [e]	$\overline{M}_{n\,th}$ [f]	$\overline{M}_w/\overline{M}_n$
D_3	$Y(OiPr)_3$	1,0	1,0	192	44	5	51	9700	9800	1,2
	$La(OTf)_3$	1,1	1,0	480	33	66	1	24000	8050	1,4
D_4	$Y(OiPr)_3$	3,2[g]	2,4	168	11	0	89	11100	3250	1,1
		3,2	2,5	432	77	3	20	12100	21500	1,5
	$Y_5O(OiPr)_{13}$[h]	2,9	2,2	432	89	3	8	22600	26300	1,5
	$La(OTf)_3$	3,2	3,0	456	30	1	69	9700	7100	1,5

[a] Time of polymerization when the polymer yield is maximum ; [b] Polymer percentage calculated from SEC analysis ; [c] Percentage of cyclic compounds other than monomer, calculated from SEC analysis ; [d] Percentage of residual monomer, calculated from SEC analysis ; [e] Number-average molecular weight of crude polymer; see experimental part for determination ; [f] Number-average molecular weight calculated from $[M]_0/[I]_0$ and conversion ; [g] at 80°C ; [h] Aggregated form of $Y(OiPr)_3$

This is far different from what was observed by several authors in the polymerization of cycles such as lactones or lactides which can be polymerized quantitatively and rapidly through a "living" process with lanthanide derivatives(5-7). Such different results might be attributed to both the low coordination ability and the low polarization of the [SiO] group compared to that of [OCO] group. Consequently, in the second part of this work, we used various rare earth compounds as additives in the conventional anionic ring-opening polymerization of cyclosiloxanes D_3 and D_4 .

Polymerization of hexamethylcyclotrisiloxane:

The polymerization of D_3 was initiated either by organolithium derivatives (*n*BuLi,Me_3SiCH_2Li) or by fluorides ($(nBu)_4NF$, $(Me_2N)_3SSiMe_3F_2$). Due to the ring strain of the monomer, with organolithium initiators, the yield in polymer is almost quantitative in a few hours at 20°C (Tab. 2). Side-reactions occur only at the end of the propagation step (8,9). Contrarily, with fluorides, the polymerization is very fast (the monomer conversion is almost quantitative within a few minutes at 20°C) but so is the occurrence of side-reactions (Tab.2). All these results are consistent with those previously published (8-10).

Tab.2. Anionic ring-opening polymerization of D_3 (**1**) either in the presence or in the absence of rare earth additives, at 20 °C ($[Ln]_0/[I]_0 = 1{,}2$)

Initiators	$[M]_0$ mol/L	Solvent	$10^2\,[I]_0$ mol/L	t (min) [a]	%Pol. [b]	%Cycl. [c]	%M [d]	$\overline{M}_{n\,exp}$ [e]	$\overline{M}_{n\,th}$ [f]	$\overline{M}_w/\overline{M}_n$
BuLi	1,0	THF	1,0	240	99,5	0,5	-	18000	22100	1,1
Me_3SiCH_2Li	1,0	Toluene [h]	1,0	1020	95,6	0,6	3,8	22150	21200	1,2
Bu_4NF	1,0	Toluene [h]	1,0	15	96	4	-	13400	21300	1,5
TASF [g]	0,75	Toluene [h]	1,8	1,5	90,8	8,5	0,7	49000	8100	1,9
Bu_4NF	1,1	Toluene [h]	1,1	22	98	1,3	0,7	10800	21750	1,3
$Y(OiPr)_3$	1,2	THF	1,1	2	76	23	1,0	6100	18400	1,4
Bu_4NF	1,0	Toluene [h]	2,2	25	96	3	1,0	5300	9500	1,7
$Nd(OiPr)_3$	1,0	THF	2,3	1,25	81	8,8	0,2	6600	7800	1,4
Bu_4NF $La(OiPr)_3$	1,0	Toluene [h]	1,0	16	97	3	-	13900	21500	1,7
TASF	0,9	Toluene [g]	1,8	1200	95	4,4	0,6	19000	10550	1,9
$Y(OiPr)_3$	1,0	THF	2,5	54	89	9,9	1,1	21100	7900	1,7

[a] Time of polymerization when the polymer yield is maximum ; [b] Polymer percentage calculated from SEC analysis ; [c] Percentage of cyclic compounds other than monomer, calculated from SEC analysis ; [d] Percentage of residual monomer, calculated from SEC analysis ; [e] Number-average molecular weight of crude polymer; see experimental part for determination ; [f] Number-average molecular weight calculated from $[M]_0/[I]_0$ and conversion ; [g] $(Me_2N)_3SSiMe_3F_2$; [h] [THF] = 0,3 mol/L coming from commercial solution

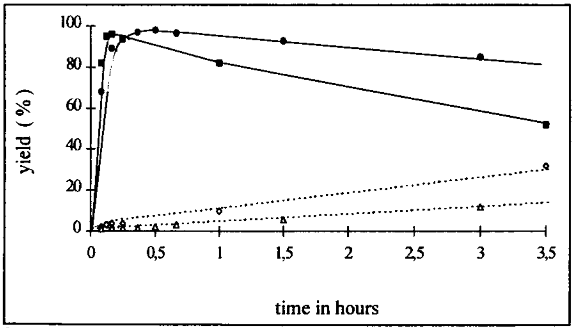


Fig. 1. Influence of the addition of $Y(OiPr)_3$ in a polymerization of D_3 initiated by $(nBu)_4NF$, at 20°C, in toluene ; $[D_3]_0 = 1{,}0$ mol/L ; $[(nBu)_4NF)]_0 = 10^{-2}$ mol/L ; $[Y(OiPr)_3]_0 = 1{,}2\ 10^{-2}$ mol/L ; [THF] = 0,3 mol/L; (■) concentration of polymer in the absence of $Y(OiPr)_3$; (◇) concentration of D_4 in the absence of $Y(OiPr)_3$; (●) concentration of polymer in the presence of $Y(OiPr)_3$; (Δ) concentration of D_4 in the presence of $Y(OiPr)_3$

In the presence of rare earth derivatives, whichever is the initiator, the rate of polymerization decreases and in general, the depolymerization reaction is highly slowered. This is particularly significant in the case of the polymerizations initiated by $(n\mathrm{Bu})_4\mathrm{NF}$ (Fig.1) and TASF. Since all polymerization rates are increased in THF versus toluene, the mechanism is still an anionic one, and not a coordinated one. Furthermore, no striking effect is observed on the molar mass of the polymer (except maybe for $\mathrm{Y(OiPr)_3}$), meaning that the rare earth compound only acts as a spectator. It is noteworthy that the rare earth addition influences not only the back-biting process (formation of cyclosiloxanes D_4, D_5, D_x...) but also the redistribution reactions. Indeed, as shown in Figure 2, the molecular weight of the polymers (at the end of the propagation reaction) is higher and the broadening of the molecular weight distribution is less important in the presence of rare earth compound than in the absence of such an additive.

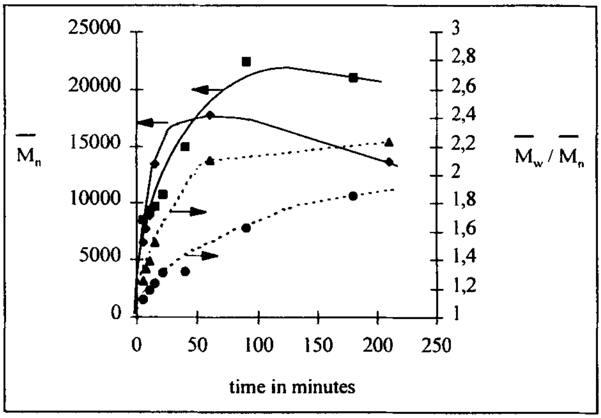
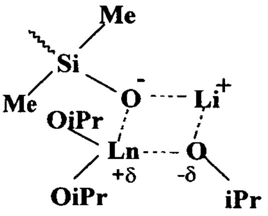


Fig. 2. Effect of $\mathrm{Y(OiPr)_3}$ addition on the number-average molecular weight ($\overline{M}_n$) and the molecular weight distribution ($\overline{M}_w / \overline{M}_n$) in a polymerization of D_3 initiated by $(n\mathrm{Bu})_4\mathrm{NF}$, at 20°C, in toluene ; $[D_3]_0 = 1{,}0$ mol/L ; $[(n\mathrm{Bu})_4\mathrm{NF})]_0 = 10^{-2}$ mol/L ; $[\mathrm{Y(OiPr)_3}]_0 = 1{,}2\ 10^{-2}$ mol/L ; [THF] = 0,3 mol/L; (◆) $\overline{M}_n$ variations versus time in the absence of $\mathrm{Y(OiPr)_3}$; (▲) $\overline{M}_w / \overline{M}_n$ variations versus time in the absence of $\mathrm{Y(OiPr)_3}$; (■) $\overline{M}_n$ variations versus time in the presence of $\mathrm{Y(OiPr)_3}$; (●) $\overline{M}_w / \overline{M}_n$ variations versus time in the presence of $\mathrm{Y(OiPr)_3}$

The behaviour observed is the same whichever are the rare earth derivative added and the amount of this additive ($[\mathrm{Ln}]_0/[\mathrm{I}]_0$ ratio). Nevertheless, when this amount is too high ($[\mathrm{Ln}]_0/[\mathrm{I}]_0 > 5$), the polymerization is completely stopped.

The reported observations might be explained assuming a complexation of the rare earth derivative on to the polysiloxane active chain ends. This complexation would decrease the charge separation of the $[\mathrm{SiO^-}...\mathrm{^+M}]$ bond (Eq.2) and, consequently, the rate of propagation. This complexation would also increase the steric hindrance around the active species and therefore, would limit the nucleophilic attack of these



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active species on the [SiO] bond of a polymer chain (inter- and intramolecular side-reactions).

This mechanism agrees with the significant decrease of the polymerization yield and the simultaneous increase of D_4 concentration observed when a non-polar solvent (toluene) is replaced by a more polar one (THF) (Fig.3). In such a case, THF could complex either on the active centers or on the rare earth derivative. This would inhibit the effect of this rare earth derivative. Futhermore, by increasing the polarity of the medium, the THF addition would increase the charge separation of the $[SiO^{-}---Li^{+}]$ bond, thus decreasing the rare earth effect.

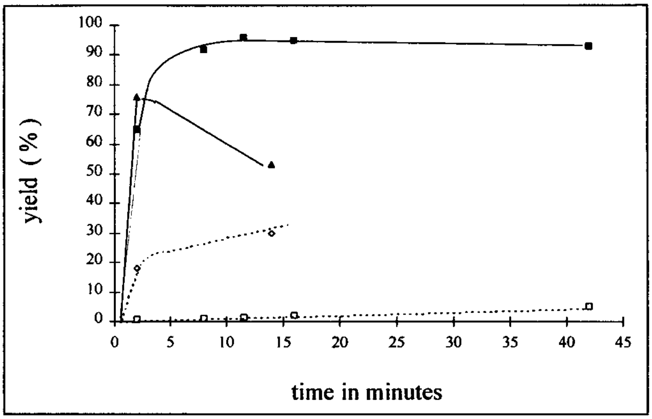

Fig. 3. Influence of the solvent in a polymerization of D_3 initiated by $(n\mathrm{Bu})_4\mathrm{NF}$, at 20°C ; $[D_3]_0 = 1{,}0$ mol/L ; $[(n\mathrm{Bu})_4\mathrm{NF}]_0 = 10^{-2}$ mol/L ; $[\mathrm{Y(OiPr)_3}]_0 = 1{,}2\ 10^{-2}$ mol/L ; [THF] = 0,3 mol/L; (▲) polymer and (◇) D_4 in THF; (■) polymer and (□) D_4 in toluene

Polymerization of octamethylcyclotetrasiloxane:

The polymerization of cyclotetrasiloxane D_4 was also initiated by both organolithium and fluoride derivatives. It was carried out at high monomer concentration ($[D_4]_0 = 2{,}6$ mol/L) and at high temperature (120°C).

In these conditions and in the absence of any additives, the yields of polymer (85% w/w) and of cyclic side-products (15%) obtained in a few hours agree with the results previously published (3,9,11). These values also agree with the theoretical one of the equilibrium concentration of D_4 at this temperature. As shown in Tab.3, in the presence of rare earth additives, the yields of polymer and of cyclic compounds are almost independent of the amount added. The only difference is a slowingdown of both polymerization and back-biting reactions which becomes more important with the amount of rare earth compounds added (Tab.4) (Fig.4).

As for the polymerization of D_3, this behaviour might be related to a complexation of the active chain ends by the rare earth atoms.

Tab.3. Anionic ring-opening polymerization of D_4 (**2**) either in the presence or in the absence of rare earth additives, at 120 °C ($[Ln]_0/[I]_0 = 1,1$)

Initiators	$10^2 [I]_0$ mol/L	$[M]_0$ mol/L	Solvent	t(h) a)	%Pol. b)	%Cycl. c)	%M d)	$\overline{M}_{n\,exp}$ e)	$\overline{M}_{n\,th}$ f)
BuLi	3,5	2,4	Toluene[h]	288	80	2	18	23000	15800
	3,8	2,6	DMF	23	85	4	11	16600	17200
Bu_4NF	3,2	3,2	-[h)]	1	81	15	4	24300	24000
TASF[g)]	2,5	2,5	Toluene[h)]	1	85	10	5	33700	25200
Bu_4NF-$Y(OiPr)_3$	2,5	2,5	Toluene[h)]	2,5	85	6	9	23300	25200
Bu_4NF-$La(OiPr)_3$	2,6	2,6	Toluene[h)]	3	84	9	7	47100	24900
Bu_4NF-$LaPO_4$	2,9	2,6	Toluene[h)]	2	86	6	8	12000	22800
BuLi-$La(OiPr)_3$	2,0	2,6	DMF	48	87	7	6	19800	33500
BuLi-$LaPO_4$	2,6	2,6	DMF	24	88	5	7	20000	26000
TASF-$Y(OiPr)_3$	2,5	2,4	Toluene[h)]	7	26	4	70	17000	6100

[a)] Time of polymerization when the polymer yield is maximum ; [b)] Polymer percentage calculated from SEC analysis ; [c)] Percentage of cyclic compounds other than monomer, calculated from SEC analysis ; [d)] Percentage of residual monomer, calculated from SEC analysis ; [e)] Number-average molecular weight of crude polymer; see experimental part for determination ; [f)] Number-average molecular weight calculated from $[M]_0/[I]_0$ and conversion ; [g)] $(Me_2N)_3SSiMe_3F_2$; [h)] [THF] = 0,3 mol/L coming from commercial solution

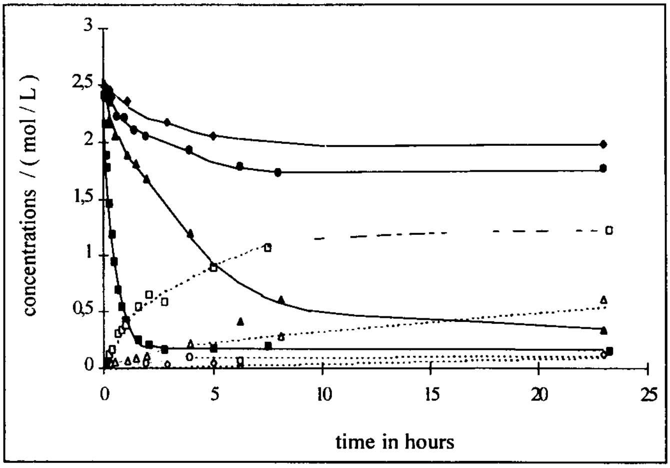

Fig. 4. Influence of the ratio r = $[Y(OiPr)_3]_0/[nBuLi]_0$ in a polymerization of D_4 initiated by nBuLi, at 120°C ; $[D_4]_0$ = 2,6 mol/L ; $[nBuLi]_0$ = 3,0 10^{-2} mol/L ; $[DMF]_0$=3,0 10^{-2} mol/L;(■) concentrations of D_4 and (□) D_x ($x \geq 5$) in the absence of $Y(OiPr)_3$; (▲) concentrations of D_4 and (Δ) D_x ($x \geq 5$) with r = 0,5 ;(●) concentrations of D_4 and (O) D_x ($x \geq 5$) with r = 1,6; (◆) concentrations of D_4 and (◇) D_x ($x \geq 5$) with r = 5

Tab.4.Influence of rare earth additives on the anionic ring-opening polymerization of D_4 (**2**), at 120 °C ; $[I]_0 = 2{,}6\ 10^{-2}$ mol/L ; $[M]_0 = 2{,}6$ mol/L ; $\overline{M_n}th = 29600$ [a]

Initiators	Solvent	$[Ln]_0/[I]_0$	t(h) [b]	%Pol. [c]	%Cycl. [d]	% M [e]	$\overline{M_n}_{exp}$ [f]
Bu_4NF - $LaPO_4$	Toluene [g]	1,1	0,1	85	7	8	13000
Bu_4NF - $La(iOPr)_3$	Toluene [g]	1,1	0,1	84	9	7	47100
Bu_4NF - $Y(iOPr)_3$	Toluene [g]	1,1	2	85	5	10	26000
Bu_4NF - $Y(iOPr)_3$	Toluene [g]	0,5	24	80	9	11	23000
Bu_4NF - $Y(iOPr)_3$	Toluene [g]	1,3	72	80	9	11	20700
Bu_4NF - $Y(iOPr)_3$	Toluene [g]	4,9	72	30	7	63	4000
BuLi - $Y(iOPr)_3$	DMF	0,5	24	80	10	10	29900
BuLi - $Y(iOPr)_3$	DMF	1,6	48	50	4	46	8100
BuLi - $Y(iOPr)_3$	DMF	5	48	50	3	47	4800

[a] Number-average molecular weight calculated from $[M]_0/[I]_0$; [b] Time of polymerization when the polymer yield is maximum ; [c] Polymer percentage calculated from SEC analysis ; [d] Percentage of cyclic compounds other than monomer, calculated from SEC analysis ; [e] Percentage of residual monomer, calculated from SEC analysis ; [f] Number-average molecular weight of crude polymer ; see experimental part for determination ; [g] [THF] = 0,3 mol/L coming from commercial solution

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