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Catalytic activity of some organolanthanoid derivatives in styrene and propene polymerization[†][‡]

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Organolanthanoids of several classes were examined as potential styrene and propene polymerization catalysts. They are: molecular hydrides of divalent lanthanoids (samarium, europium, ytterbium); naphthalene and stilbene complexes of neodymium(III), samarium(II), europium(II), ytterbium(II), lutetium(III); amides and alkoxides (including heterobifunctional derivatives) of praseodymium(III), neodymium(III), samarium(II), europium(II), thulium(III), ytterbium(II, III); thiolate of samarium(III); phenyl and phenylethinyl derivatives of europium(II), thulium(III), ytterbium(II); methylytterbium cluster $Yb_8(\mu\text{-}CH_3)_{14}(\mu\text{-}CH_2)(THF)_6$; heterobimetallic samarium(II), ytterbium(II, III) complexes; diazabutadiene ytterbium(III) derivatives; metallic praseodymium and ytterbium, activated by iodine. The highest activity in styrene polymerization revealed hydrides, naphthalene and stilbene complexes of samarium(II), europium(II) and ytterbium(II). In the propene polymerization only $[(\eta^5\text{-}C_5H_4)CH_2CH(CH_2OBu)(\eta^1\text{-}O)]YbMe(THF)$ displayed noticeable activity. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

Several classes of organolanthanoid derivatives are known to be catalysts of olefin polymerization.[1] Unlike most of *d*-element-based catalysts, the organolanthanoid-derivative-mediated catalytic processes do not require a co-catalyst presence. The highest catalytic activity in α-olefin polymerization showed cyclopentadienyl complexes of Cp_2LnR type, where R = H or alkyl.[2] Active species of similar type are evidently formed in two-component systems Cp_2LnCl/LiR[3] and $(C_5H_3Bu^t{}_2\text{-}1,3)_2Yb/AlH_3$.[4] Scandium complex containing Sc—Si function, $Cp_2Sc[Si(SiMe_3)_3](THF)$, polymerizes ethene under mild conditions but is inactive towards propene.[5] Cationic complexes of yttrium $(C_5H_4SiMe_3)_2Y[BMe(C_6F_5)_3]$ and $(C_5H_5)_2Y[BMe(C_6F_5)_3]$ were employed in isobutene polymerization.[6] The catalytic activity of Ln(II) derivatives was studied only with a few examples. The non-solvated decamethylsamarocene complex $(C_5Me_5)_2Sm$ was investigated by Evans *et al.* in the propene, penten-1 and hexen-1 co-polymerization with ethene.[7] It was established that the ytterbium complex $(1,2\text{-}Bu^t{}_2C_5H_3)_2Yb$ polymerizes ethene and styrene.[8] The non-cyclopentadienyl series derivatives naphthalene and anthracene complexes of ytterbium(II) $C_{10}H_8Yb(THF)_3$ and $C_{14}H_{10}Yb(THF)_3$, under mild conditions catalyze isoprene, piperylene and methyl methacrylate polymerization.[9] Many other classes of organolanthanoids remain out of sight of investigators as plausible catalysts for unsaturated hydrocarbons polymerization.

In order to close this gap partially, we carried out a qualitative determination of the catalytic activity of some of the organolanthanoid series, as well as lanthanoid metals and their iodides, in α-olefins polymerization. Styrene and propene were chosen as the test monomers because the former is easily polymerized ionically, and the latter, though unable

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to polymerize under ionic conditions, can be polymerized with organometallic or free-radical initiators. We explored as polymerization precursors the molecular hydrides of divalent samarium, europium and ytterbium, amides, alkoxides and thiolates of lanthanoids, homo- and hetero-metallic clusters, complexes containing naphthalene, stilbene, phenyl, phenylethinyl, fluorenyl (Flu) and indenyl (Ind) ligands, half-sandwich complexes with heterobifunctional cyclopentadienyl-substituted alcohol, amine and siloxane. Polymerization tests were conducted at room temperature without solvent for styrene or in toluene medium in the case of propene. Catalyst concentration was 3–5% of monomer weight. The data obtained are summarized in Table 1.

EXPERIMENTAL

THF, toluene, styrene, benzene and propene were purchased at Ecros Company (St. Petersburg, Russia). Toluene was distilled from ketyl benzophenone before polymerization reaction. Styrene was dried over molecular sieves 5A. Before the polymerization tests, propene was passed over columns filled with molecular sieves 3A and bubbled throw a trap filled with tri-*iso*-butylaluminum. Molecular weights were measured by the viscousimetric method in benzene at room temperature. All the compounds tested in polymerization were obtained according to published strategies: **1** and **2**;[10] **3**;[11] **4** and **5**;[9] **6**;[12] **7**;[13] **8** and **10**;[14] **9**;[15] **11–33**;[1] **19**;[15]; **36**;[16] **38**;[17] **39**;[18] **44**;[19] **45**.[20] The composition and structure of recently obtained complexes **34, 35, 37, 40** and **41** were confirmed by microanalysis, IR and NMR spectroscopy and X-ray analysis. Their syntheses will be described elsewhere.

Styrene and propene polymerization tests were performed under vacuum using the standard Schlenk technique except for the experiments with propene polymerization at 10 atm, which were carried out in a stainless steel flask.

Styrene polymerization

An evacuated Schlenk tube equipped with a magnetic stir bar was charged with 2.7 g of styrene and 0.09 g of compound **1**. The reaction mixture was mixed at room temperature for a day. The polymer formed was dissolved in THF and 0.5 ml of methanol was added to a solution to decompose the catalyst. The mixture was filtered through a glass filter and polymer was precipitated with 30 ml of methanol. These conditions were used for testing of all the other compounds indicated in Table 1.

Propene polymerization

10 ml of toluene solution of compound **41** (0.018 g) was placed in a tube of 350 ml volume equipped with a magnetic stir bar. 350 ml (1.2 atm, 25 °C) of gaseous propene was condensed to a mixture and the tube was sealed. The mixture was stirred at room temperature for a day and then the catalyst was decomposed by adding methanol (0.5 ml). Then the mixture was filtered and 30 ml of methanol was added to precipitate the polymer formed. These conditions were used for a check of the catalytic activity of all the compounds listed in Table 1 in propene polymerization under atmospheric pressure.

Propene polymerization under enhanced pressure

Into a stainless steel container of 100 ml volume equipped with manometer and unit for gas loading, 10 ml of toluene and a sealed thin-walled glass tube containing 0.11 g of compound **3** were placed. Gaseous propene was added to the container up to a pressure of 10 atm. The vessel was disconnected from the propene line and shaken to break the glass tube. The mixture obtained was held at room temperature for a day. The subsequent procedure to check for polymer formation and its isolation were performed as indicated above. The experiments with compounds **1** and **2** were performed in the same way.

RESULTS AND DISCUSSION

As was supposed, owing to the high degree of ionicity of the organolanthanoid derivatives and the high electrode potential of these metals, most of the lanthanoid complexes listed in Table 1 initiate styrene polymerization. High catalytic activity revealed the hydrides **1–3**. In their presence the reactions proceeded within 5–8 h with a complete conversion of styrene. Europium complex **2** gave the polymer with the highest molecular weight 1×10^6. The molecular weights of polystyrene formed with ytterbium **3** and samarium **1** hydrides were noticeably lower 3×10^5 and 1.5×10^5, respectively. The decreasing molecular weights of the polymers in going from europium to ytterbium

Table 1 Styrene and propene polymerization catalyzed by organolanthanoid derivatives.

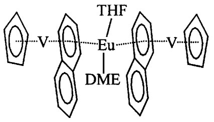
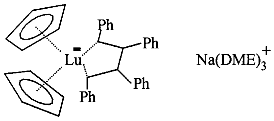
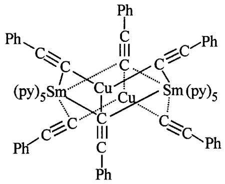
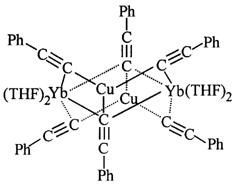
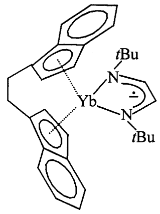
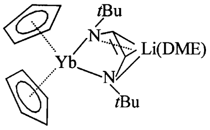
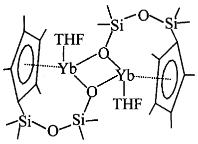
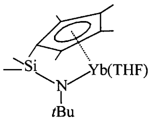
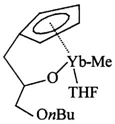
		Conversion	
Compound no.	Catalyst	Styrene	Propene
1	$SmH_2(THF)_2$	100	0^a
2	$EuH_2(THF)_2$	100	0^a
3	$YbH_2(THF)_2$	100	0^a
4	$C_{10}H_8Eu(THF)_3$	100^b	0
5	$C_{10}H_8Yb(THF)_3$	100^b	0
6		27	—
7	$[NdCl_2(THF)_2]_nC_{10}H_8LiCl$	0	0
8	$(PhCHCHPh)Sm(THF)_3$	100^b	0
9	$(PhCHCHPh)Yb(THF)_3$	100^b	0
10		22	0
11	$[(Me_3Si)_2N]_2Sm(DME)_2$	5	—
12	$[(Me_3Si)_2N]_2Eu(DME)$	100	0
13	$[(Me_3Si)_2N]_2Yb(DME)$	41	—
14	$[(Me_3Si)_2N]_3Pr$	0	—
15	$[(Me_3Si)_2N]Pr(SC_4H_9)_2$	0	—
16	$[(Me_3Si)_2N]_2Sm(SC_4H_9)$	0	—
17	$(C_4H_9S)_3Sm$	0	—
18	$(Bu^tO)_2Eu$	100	0
19	$(2,4,6\text{-}Bu^t{}_3C_6H_2O)_2Yb(THF)$	40	—
20	$(Bu^tO)_3Nd$	13	—
21	$(Bu^tO)NdI_2(THF)_4$	0	—
22	$(PhO)_3Tm(DME)_2$	5	—
23	$(PhC{\equiv}C)EuI(DME)$	18	—
24	$(PhC{\equiv}C)_2Yb(DME)$	70	—
25	$Ph_2Yb(THF)_2$	50	—
26	$Yb_8(\mu\text{-}CH_3)_{14}(\mu\text{-}CH_2)(THF)_6$	—	0
27	$Ph_3Tm(THF)_3$	—	0
28		0	—
29		27	—
30	$(Ph_3Ge)_2Yb(THF)_4$	—	0
31	$(Ph_3Sn)_2Yb(THF)_4$	—	0
32	$Cp_2Yb\{Hg[Ge(C_6F_5)_3]_3\}$	—	0
33	$Cp_2Yb(THF)$	14	—
34	$Ind_2Yb(THF)_2$	5	<5

Table 1 Continued.

Compound no.	Catalyst	Conversion	
		Styrene	Propene
35	$Flu_2Yb(THF)_2$	—	<5
36	$Cp_2Yb(DAD)$	0	0
37		—	0
38		—	0
39		—	Traces
40		—	Traces
41		9	10
42	$Pr(MeT) + I_2$	60	0
43	$Yb(MeT) + I_2$	37	—
44	$SmI_2(THF)_2$	76	—
45	$TmI_2(DME)3$	20	0

[a] 10 atm pressure of propene.
[b] Reaction proceeded for 5 min.

and samarium hydrides coincides with an increase of the standard potential of Ln(II)/Ln(III) transfer in the series europium (0.34 V), ytterbium (1.18 V) and samarium (1.50 V) and probably indicates an increasing catalytic activity of the compounds in the same sequence.

The complexes **4, 5, 8** and **9**, containing Ln^{2+} cations and naphthalene $(C_{10}H_8)^{2-}$ or stilbene $(PhCHCHPh)^{2-}$ dianions displayed the highest activity in styrene polymerization. In these cases the polymerization proceeded exothermally and finished in a few minutes to give a polymer with $M_w = 3–5 \times 10^5$. It is of interest that compound **6** containing the Eu^{2+} cation and the formally neutral naphthalene ligand,[12] is essentially less active. Polymerization with this complex being carried out for 20 h yielded less than 30% of low molecular weight ($M_w = 3 \times 10^4$) polystyrene. The naphthalene and stilbene *ate*-complexes **7** and **10** were almost inactive under the given conditions.

Among the amides (**11–15**) and thiolate–amides (**15–17**) only the derivatives of divalent metals, compounds **11–13**, exhibited some activity in styrene polymerization. In contrast to hydrides **1–3**, the activity of the amides decreased from europium to ytterbium and samarium derivatives. This may be explained by different mechanisms of initiation for hydride and amide complexes. The same pattern takes place in the group of alkoxides **18–22**. Europium(II) *tert*-butoxide **18** yielded 100% conversion, whereas the neodymium(III) analogue **20** gave only 13% of polymer, but thulium(III) phenoxide **22** was factually inactive under the same conditions. Feeble catalytic properties were displayed by diphenylethinyl, cyclopentadienyl and indenyl complexes **23–25, 28, 29, 33, 34, 36**. It is interesting to note that complex **41**, containing both the η^5:η^1-heterobifunctional ligand $C_5H_4CH_2CH(CH_2OBu)O$ and the ancillary active Yb—Me function yielded only 9% conversion in styrene polymerization, although it transpired that this compound was the only complex among those listed in Table 1 that exhibited appreciable activity toward propene.

Halogen-activated metals including rare earth elements[21] are known to display high reactivity toward organic and organometallic substrates. We have found with the example of praseodymium and ytterbium that lanthanoid metals are able to initiate olefin polymerization. The degree of styrene conversion in trials **42** and **43** did not exceeded 40–60%, but evidently it might be enhanced by selection of the reaction conditions. A similar activity has been shown for iodides of samarium(II) **44** and thulium(II) **45**. Surprisingly, the thulium derivative, though possessing a higher reduction potential (2.20 V) than samarium (1.50 V), was less active.

It was found that all of complexes explored were inert toward propene under the given conditions. Such a low activity may be explained by the lack of Ln—R or Ln—H functions, which in most cases are responsible for initiation of polymerization. Compound **41**, the only one containing a methyl group bonded to ytterbium, yielded 10% of polypropene. The inactivity of molecular hydrides **1–3**, unlike the known catalysts of Cp_2LnH type, is concerned apparently with their low solubility in toluene. We anticipate the same factor being responsible for the absence of catalytic activity in the case of the methyl–ytterbium cluster **26** and cationic complex **32**.

CONCLUSION

It is found that the molecular hydrides $LnH_2(THF)_2$, the naphthalene $C_{10}H_8Ln(THF)_3$ and stilbene $(PhCHCHPh)Ln(THF)_3$ complexes of divalent samarium, europium and ytterbium, as well as amide $[(Me_3Si)_2N]_2Eu(DME)$ and alkoxide $(Bu^tO)_2Eu$, are efficient catalysts in styrene polymerization. Only one of the various types of compound studied initiates propene polymerization: that compound is ytterbium derivative $[(\eta^5\text{-}C_5H_4)CH_2CH(CH_2OBu)(\eta^1\text{-}O)]YbMe(THF)$, containing a heterobifunctional ligand and ancillary Yb—Me group, which revealed noticeable activity at room temperature and 1.2 atm of propene.

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REFERENCES

1. Britovsek GJP, Gibson VC, Wass DF. *Angew. Chem. Int. Ed. Eng.* 1999; **38**: 429; Margl P, Deng L, Ziegler T. *J. Am. Chem. Soc.* 1999; **121**: 154; Bochkarev MN, Zakharov LN, Kalinina GS. In *Organoderivatives of Rare Earth Elements*, Kluwer: Dordrecht, 1995; 535.
2. Watson PL. *J. Am. Chem. Soc.* 1982; **104**: 337; Watson PL, Parshall GW *Acc. Chem. Res.* 1985; **18**: 51; Den Haan KH, Wielstra Y, Eshnis JJW, Teuben JH *J. Organomet. Chem.* 1987; **323**: 181; Stern D, Sabat M, Marks T. *J. J. Am. Chem. Soc.* 1990; **112**: 9558; Burger BJ, Thompson ME, Cotter WD, Bercaw JE. *J. Am. Chem. Soc.* 1990; **112**: 1566; Schaverien CJ *Organometallics* 1994 **13**: 69; Shapiro PJ, Cotter WD, Schaefer WP, Labinger JA, Bercaw JE. *J. Am. Chem. Soc.* 1994; **116**: 4623; Jeske G, Lauke H, Mauermann H, Swepstone PN, Schumann H, Marks TJ. *J. Am. Chem. Soc.* 1995; **107**: 8091; Jeske G, Lauke H, Mauermann H, Schumann H, Marks TJ *J. Am. Chem. Soc.* 1995; **107**: 8103.
3. Kvostov AV, Belsky VK, Sizov AI, Bulychev BM, Ivchenko NB *J. Organomet. Chem.* 1998; **564**: 5.
4. Knjazhanski SYa, Kalyuzhnaya ES, Herrera LEE, Bulichev BM, Khvostov AV, Sizov AI *J. Organomet. Chem.* 1997; **531**: 19.
5. Campion BK, Heyn RH, Don Tilley T *Organometallics* 1993; **12**: 2584.
6. Song X, Thornton-Pett M, Bochmann M *Organometallics* 1998 **17**: 1004.
7. Evans WS, De Coster DM, Greaves J *Organometallics* 1996 **15**: 3210.
8. Kvostov AV, Sizov AI, Bulychev BM, Knjazhanski SYa, Belsky VK *J. Organomet. Chem.* 1998; **559**: 97.
9. Bochkarev MN, Trifonov AA, Fedorova EA, Emelyanova NS, Basalgina TA, Kalinina GS, Razuvaev GA. *J. Organomet. Chem.* 1989; **372**: 217.
10. Trifonov AA, Fedorova EA, Kirillov EN, Bochkarev MN *Izv. Acad. Nauk. Ser. Him.* in press.
11. Bochkarev MN, Fedorova EA, Penyagina IM, Vasina OA, Horshev SYa, Protchenko AV. *Metalloorg. Him.* 1989; **2**: 703.
12. Fedushkin IL, Nevodchikov VK, Cherkasov VK, Boch-

karev MN, Schumann H, Girgsdies F, Gorlits FH, Kociok-Kohn G, Pickardt J. *J. Organomet. Chem.* 1996; **511**: 157.

13. Kirillov EN, Trifonov AA, Nefedov SE, Eremenko IL, Edelmann FT, Bochkarev MN *Z. Naturforsch. Teil B* 1999; **54**: 1379.
14. Trifonov AA, Kirillov EA, Fedorova EA, Bochkarev MN, Girgsdies F, Schumann H. *Izv. Acad. Nauk. Ser. Him.* in press.
15. Trifonov AA, Kirillov EN, Bochkarev MN, Schumann H, Muehle S. *Izv. Acad. Nauk. Ser. Him* 1999; **2**: 384.
16. Trifonov AA, Kirillov EN, Fedorova EA, Makarenko NP, Bochkarev MN, Schumann H, Muehle S *Izv. Acad. Nauk. Ser. Him.* 1998; **11**: 2345.
17. Trifonov AA, Zakharov LN, Bochkarev MN, Struchkov YuT *Izv. Acad. Nauk. Ser. Him.* 1994; **1**: 148.
18. Trifonov AA, Kirillov EN, Fischer A, Edelmann FT, Bochkarev MN *J. Chem. Soc. Chem. Commun.* 1999; 2203.
19. Kagan HB, Namy JL *Tetrahedron* 1986 **42**: 6573.
20. Bochkarev MN, Fedushkin IL, Fagin AA, Petrovskaya TV, Ziller JW, Broomhall-Dillard RNR, Evans WJ *Angew. Chem. Int. Ed. Engl.* 1997; **36**: 133.
21. Bochkarev LN, Molosnova NE, Zakharov LN, Fukin GK, Yanovsky AI, Struchkov YuT. *J. Organomet. Chem.* 1995; **485**: 101; Bochkarev LN, Stapntseva TA, Zakharov LN, Fukin GK, Yanovsky AI, Struchkov YuT. *Organometallics* 1995; **14**: 2127.