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Polymerization of Isoprene by a Single Component Lanthanide Catalyst Precursor

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Since the main component of natural rubber is *cis*-1,4-polyisoprene, catalysts that can convert isoprene stereospecifically into this polymer without *trans*-1,4-polyisoprene or 1,2-polyisoprene contaminants are highly valued. Although many initiators will polymerize butadiene and isoprene including elemental alkali metals and metal alkyls,[1−4] one of the best catalytic systems in the literature for formation of *cis*-1,4-polyisoprene is lanthanide-based and uses neodymium.[5−13] Although neodymium catalysts can provide >98% *cis*-1,4-polyisoprene as well as high *cis*-1,4-polybutadienes, the procedure for preparing active catalysts is complicated and not well understood. The complexity of typical neodymium catalyst systems makes it difficult to study, understand, and modify these effective catalysts.

Neodymium catalysts are typically prepared from a ternary system involving a Nd(III) salt, an ethylaluminum chloride (Et_2AlCl or $EtAlCl_2$) or other chloride sources, and an isobutylaluminum compound (Al^iBu_3 or AlH^iBu_2).[6,14−18] However the protocols in the literature vary in terms of the sequence of addition of the activators and the amount of time and temperature needed to age the catalyst for optimum performance. Systems utilizing previously prepared neodymium chloride and Al^iBu_3 or AlH^iBu_2 have also been reported.[9,19]

We report here that high *cis*-1,4-polyisoprene can be generated starting with a simple single component lanthanide initiator which is neither an elemental metal nor a metal alkyl. This breakthrough was made possible by the discovery of the first molecular complexes of Tm(II),[20] Dy(II),[21] and Nd(II).[22] These new highly reducing oxidation states have recently provided advances in both organometallic and dinitrogen chemistry.[23,24] We now report their utility in polymerization chemistry.

In the course of investigating the polymerization reactivity of TmI_2, DyI_2, and NdI_2, it was discovered that these divalent lanthanide diiodides can initiate polymerization of isoprene to high *cis*-1,4-polyisoprene without any additives. This discovery triggered a broader examination of the reactivity of LnI_2 complexes with isoprene. Polymerizations were examined both with and without alkylaluminum activators (Scheme 1) since alkylaluminum compounds are commonly included in polymerization procedures to remove impurities.

Polymerizations were performed by either of two experimental protocols. In one case, the lanthanide initiator was added to a solution of isoprene in hexane in a glovebox.[25] Polymerization could also be done outside a glovebox by syringing isoprene into a vial that had previously been charged with lanthanide initiator.[26] Reactions were typically allowed to run overnight, after which the solutions were quenched with 0.1% BHT in 2-propanol. The polymers were subsequently washed with a 5% HCl solution. Residual solvent was allowed to evaporate, and the polymers were further dried under vacuum at 10^{-3} Torr. The polymers were analyzed by size exclusion chromatography and ^{13}C NMR spectroscopy.[27]

Scheme 1

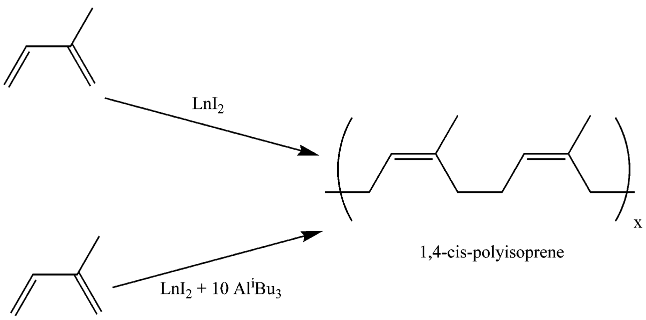

Table 1. Polymerization of Isoprene by LnI_2 (Ln = Nd, Sm, Dy, Tm) and $LnI_2(THF)_x$ (Ln = Sm, Tm)

catalyst precursor	cocatalyst	Al:Ln ratio	grams of polymer	M_w ($\times 10^3$)[a]	poly-dispersity[b]
NdI_2	none	0	0.856	400	3.3
SmI_2	none	0	0.956	1900	2.2
$SmI_2(THF)_x$	none	0	0.900	1300	2.5
DyI_2	none	0	1.05	3000	1.5
TmI_2	none	0	0.601	200	2.4
$TmI_2(THF)_x$	none	0	0.787	1000	2.0
NdI_2	Al^iBu_3	10	1.51	500	2.2
SmI_2	Al^iBu_3	10	1.66	2100	1.2
$SmI_2(THF)_x$	Al^iBu_3	10	1.55	1500	2.2
DyI_2	Al^iBu_3	10	1.46	200	2.9
TmI_2	Al^iBu_3	10	1.72	2300	4.0
$TmI_2(THF)_x$	Al^iBu_3	10	1.81	2800	3.0

[a] Molecular weight was determined by SEC. [b] Polydispersity was determined by SEC.

The results of the polymerization runs are given in Table 1. TmI_2,[28] DyI_2,[21] and NdI_2[29] all initiate polymerization of isoprene without any additives. Since the unsolvated diiodides appear to be insoluble in hexane, this reaction appears to be heterogeneous, and it is unlikely that either the molecular weights or polydispersities are optimized. The brown, purple, and black colors of TmI_2, DyI_2, and NdI_2, respectively, are maintained during the polymerization and only changed to yellow upon quenching with BHT/2-propanol. After the HCl wash, the polymers are white.

Surprisingly, the less powerful reductant, SmI_2,[30] also initiates the polymerization of isoprene without any additive. SmI_2 has been examined extensively as a polymerization initiator[31,32] but has not been studied with isoprene to our knowledge.

Since $SmI_2(THF)_x$ and $TmI_2(THF)_x$ are the precursors to the unsolvated LnI_2 complexes described above, these THF solvated systems were also examined as initiators. Although the presence of THF generally inhibits polymerization with lanthanides since it effectively blocks coordination sites,[33] purple $SmI_2(THF)_x$[34] ($x = 2$) and brown $TmI_2(THF)_x$[35] ($x = 1.8-2.4$) were both found to initiate isoprene polymerization to form polymers of molecular weight and polydispersity similar to those of the THF-free systems. As in the unsolvated systems,

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these precursors were not soluble in hexanes, and their colors did not change during polymerization.

The reactivity of the LnI_2 initiators was also examined in the presence of Al^iBu_3, a common activator in lanthanide-based isoprene polymerizations.[5−7] TmI_2, DyI_2, NdI_2, and SmI_2 all initiate polymerization in the presence of 10 equiv of Al^iBu_3. The additive seems to enhance the solubility of the system, and the polymerizations appear to proceed faster. The yields were also enhanced in the presence of the alkylaluminum reagent. $SmI_2(THF)_x$ and $TmI_2(THF)_x$ also generate polyisoprene in the presence of Al^iBu_3, but in the case of Sm, the originally purple solid turns green upon addition of the organoaluminum reagent. This could be due to desolvation.[36]

In all cases the isolated polymers were found to be high *cis*-1,4-polyisoprene by ^{13}C NMR spectroscopy. No evidence of a trans polymer was observed.

These results show that very simple lanthanide reagents can be used to polymerize isoprene. Multicomponent catalysts are not necessary. In addition, these LnI_2 precursors have some advantages over conventional catalysts made from trivalent lanthanide salts, since they can be made directly from the metal and iodine[20−22] and require no dehydration of the precursor salts. These results indicate that the utility of LnI_2 complexes in polymerization chemistry should be explored more extensively, especially with the new divalent Tm, Dy, and Nd systems.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) For alkylaluminum-free reactions, LnI_2 (20 mg) was added to a 20 mL vial containing isoprene (3 mL, 30 mmol) and 5 mL of hexanes in a nitrogen-containing glovebox. In the other cases, LnI_2 (20 mg) was added to a 20 mL vial containing isoprene (3 mL, 30 mmol), 5 mL of hexanes, and 10 equiv of Al^iBu_3 in a nitrogen-containing glovebox. After the suspension was stirred overnight at room temperature, a thick mixture formed. Evaporation of the hexanes leaves an elastomer. The elastomer was quenched with 0.1% BHT in 2-propanol and 1 mL of 5% hydrochloric acid.
(26) A vial was charged with LnI_2 (20 mg), 5 mL of hexanes, and a stir bar in a nitrogen-containing glovebox. The vial was sealed with a septum and removed from the glovebox. For alkylaluminum-free reactions, isoprene (3 mL, 30 mmol) was added via syringe. In the other cases, 10 equiv of Al^iBu_3 and then isoprene (3 mL, 30 mmol) were added via syringe. After the suspension was stirred overnight at room temperature, a thick mixture formed. Evaporation of the hexanes leaves an elastomer. The polymer was isolated as described in ref 25.
(27) See Supporting Information.
(28) A brown powder of $TmI_2(THF)_x$[35] (2 g, 3.5 mmol) was placed in a 320 mm × 25 mm glass reaction tube fitted with a 24/40 joint and a high-vacuum greaseless stopcock adapter. The tube was heated to 150 °C for 18 h under high vacuum (4×10^{-7} Torr) to yield TmI_2 as a brown powder (1.49 g, 100%). Complexometric analysis:[37] Calcd for TmI_2: Tm, 40.0. Found: Tm, 39.8.
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