Chloride Effects in Lanthanide Carboxylate Based Isoprene Polymerization

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Introduction

The development of new variations of traditional elastomers of butadiene,[1,2] isoprene, and their blends has grown in importance as demands for high-performance synthetic rubbers have increased.[3−5] Blended elastomers can have enhanced physical and mechanical properties that provide better processing as well as significant cost saving. For example, blends can have improved flex fatigue resistance, abrasion resistance, and lower heat buildup, which are all of importance for high-performance tires.[3,6] One blend involves adding *trans*-1,4-polyisoprene to natural rubber, the bulk of which is *cis*-1,4-polyisoprene, since these components have comparable glass transition temperatures and the mixture has excellent processability and mechanical properties.[7,8]

As part of our investigation of the highly efficient polymerization of isoprene to >98% *cis*-1,4-polyisoprene using lanthanide catalysts, we have sought to eliminate some of the uncertainties in the composition of the catalysts by using fully characterized lanthanide carboxylate precursors.[9] Two types of neodymium-based catalysts generally are used to perform the stereoselective polymerization of dienes to *cis*-1,4-polydienes: a ternary system that involves a mixture of neodymium carboxylates, an ethylaluminum chloride reagent, and triisobutylaluminum or isobutylaluminum hydride[10−17] and a binary system that involves neodymium trichloride and triisobutylaluminum.[18,19] Some reports in the literature suggest that the ethylaluminum chloride in the ternary system reacts with the neodymium carboxylates to form $NdCl_3$, in analogy to Ziegler−Natta formation of $TiCl_3$. This is consistent with the success of the binary system starting with $NdCl_3$. However, by using well-defined lanthanide carboxylates, it has been shown that the Et_2AlCl reaction intermediate is not simply $NdCl_3$ but a more complicated compound containing carboxylate, ethyl, and chloride groups as well as aluminum.[9]

Both ternary and binary systems in the literature use an isobutylaluminum reagent to make an active catalyst. Generally, a 10−30-fold excess of the isobutylaluminum is used, but with the fully defined carboxylate precursors, stoichiometric isobutylaluminum is sufficient.[9] In all cases, chloride is included and this is generally believed to be crucial to the success of the polymerization.[10−21]

Since ternary catalysts generally start with carboxylate precursors and binary catalysts start with chloride precursors, direct comparison of the two catalyst preparation protocols using the same starting materials has not been reported to our knowledge. In addition, the carboxylate precursors are generally mixtures of isomers and may also contain carboxylic acid residues. We report here a comparison of ternary and binary systems using the same fully characterized lanthanide carboxylates as starting materials. This allows a direct evaluation of chloride and chloride-free systems. In the latter case, an interesting blend of *cis*- and *trans*-1,4-polyisoprene is obtained.

Results

Ternary System. The neodymium and lanthanum tris-2,2-dimethylbutyrate precursors, $\{Nd[O_2CC(Me)_2Et]_3\}_x$, **1**, and $\{La[O_2CC(Me)_2Et]_3\}_x$, **2**, were treated with 2.5 equiv of Et_2AlCl to form materials which contain a 2:1:5 Ln:Al:Cl molar ratio by elemental analysis.[9] The solids were isolated and reacted in hexane with 1 equiv of AlR_3 ($R_3 = Me_3$, Et_3, ${}^iBu_3$, H^iBu_2) in a glovebox free of coordinating solvents. Isoprene was added, and a plug of polymer formed in less than 1 h. The mixture was quenched with 0.1% butylated hydroxytoluene (BHT) in 2-propanol, and the product was washed with a 5% aqueous HCl solution. Residual solvent was allowed to evaporate, and the polymers were further dried under vacuum at 10^{-3} Torr. Polymerizations were also run for extended periods of time after the initial buildup of polyisoprene with no significant change in the properties of the polymer.

The polymers were characterized as *cis*-1,4-polyisoprene by ^{13}C NMR spectroscopy (Scheme 1). There was no evidence for the trans polymer in the NMR spectra, and hence, within the NMR limits, this polymer is high cis.[2] The polymers were analyzed by gel permeation chromatography (GPC) and found to have a monomodal molecular weight distribution. The weight-average molecular weight of the polyisoprene (Table 1) did not differ significantly when either the lanthanide, Nd or La, or the initiator, AlR_3 ($R_3 = Me_3$, Et_3, ${}^iBu_3$, H^iBu_2), was varied. Polydispersities were more variable. The lowest polydispersity was observed with $AlEt_3$ and the highest with HAl^iBu_2, but none of the molecular weights were optimized in terms of mixing time, speed, and temperature.

Binary System. In this catalytic procedure, the tris-2,2-dimethylbutyrate precursors used in the ternary system, **1** and **2**, were treated directly with 3 equiv of AlR_3 ($R_3 = Me_3$, Et_3, ${}^iBu_3$, H^iBu_2). Isoprene was added, and the polymerizations were run overnight. The neodymium solution was light green, the lanthanum solution was colorless, and the polymeric products were soluble in hexane. ^{13}C NMR spectroscopy showed that the polymers generated in this binary system were a mixture of *cis*- and *trans*-1,4-polyisoprene (Scheme 2),[2] and GPC analysis revealed a bimodal molecular weight distribution. Again, the average molecular weight of the polyisoprene (Table 1) did not differ significantly when either the lanthanide, Nd or La, or the initiator, AlR_3 ($R_3 = Me_3$, Et_3, ${}^iBu_3$, H^iBu_2), was varied, but all of the molecular weight values were slightly higher than those in the ternary systems. As in the ternary system, polydispersities were more variable, but the polymerizations were not optimized in terms of mixing time, speed, and temperature.

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Scheme 1

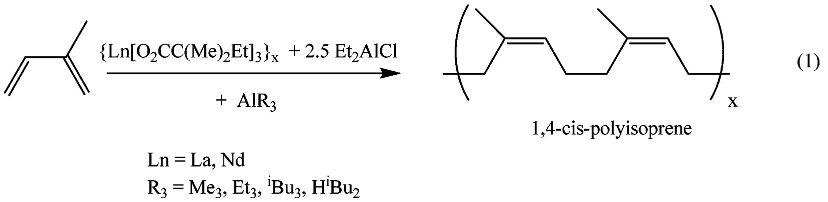
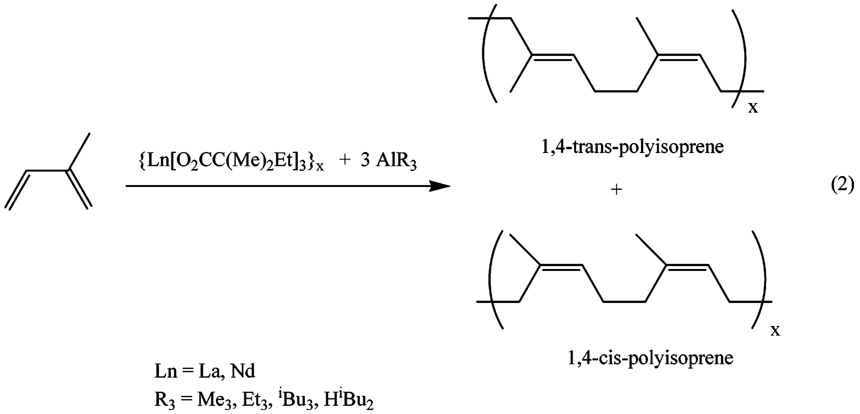


Table 1. Polymerization of Isoprene by Ternary and Binary Lanthanide Catalytic Systems

precursor	cocatalyst	time (h)	M_w ($\times 10^3$)[a]	polydispersity[a]	distribution[b]
$\{Nd[O_2CC(Me)_2Et]_3\}_x/2.5Et_2AlCl$	$AlMe_3$	1	1000	4.2	m
$\{Nd[O_2CC(Me)_2Et]_3\}_x/2.5Et_2AlCl$	$AlEt_3$	1	1200	2.9	m
$\{Nd[O_2CC(Me)_2Et]_3\}_x/2.5Et_2AlCl$	AlH^iBu_2	1	700	13.5	m
$\{Nd[O_2CC(Me)_2Et]_3\}_x/2.5Et_2AlCl$	Al^iBu_3	1	1000	7.2	m
$\{La[O_2CC(Me)_2Et]_3\}_x/2.5Et_2AlCl$	$AlMe_3$	1	1200	7.1	m
$\{La[O_2CC(Me)_2Et]_3\}_x/2.5Et_2AlCl$	$AlEt_3$	1	1200	2.6	m
$\{La[O_2CC(Me)_2Et]_3\}_x/2.5Et_2AlCl$	AlH^iBu_2	1	900	7.6	m
$\{La[O_2CC(Me)_2Et]_3\}_x/2.5Et_2AlCl$	Al^iBu_3	1	1000	5.2	m
$\{Nd[O_2CC(Me)_2Et]_3\}_x/2.5Et_2AlCl$	3 $AlMe_3$	18	1500	14.3	b
$\{Nd[O_2CC(Me)_2Et]_3\}_x$	3 $AlEt_3$	18	1500	11.6	b
$\{Nd[O_2CC(Me)_2Et]_3\}_x$	3 AlH^iBu_2	18	1200	19.1	b
$\{Nd[O_2CC(Me)_2Et]_3\}_x$	3 Al^iBu_3	18	1300	19.8	b
$\{La[O_2CC(Me)_2Et]_3\}_x$	3 $AlMe_3$	18	1700	9.6	b
$\{La[O_2CC(Me)_2Et]_3\}_x$	3 $AlEt_3$	18	1500	9.8	b
$\{La[O_2CC(Me)_2Et]_3\}_x$	3 AlH^iBu_2	18	1300	20.2	b
$\{La[O_2CC(Me)_2Et]_3\}_x$	3 Al^iBu_3	18	1800	4.9	b

[a] Determined by GPC. [b] m = monomodal; b = bimodal.

Scheme 2



Discussion

Polymerization of isoprene with ternary systems comprised of fully characterized lanthanide tris-2,2-dimethylbutyrates, $\{Ln[O_2CC(Me)_2Et]_3\}_x$, Et_2AlCl, and an R_3Al initiator formed high *cis*-1,4-polyisoprene in a manner similar to literature preparations starting with neodymium carboxylate salts of mixed isomeric composition and carboxylic acid content. One significant difference is that only 1 equiv of the R_3Al initiator is needed compared to the excess usually used. In the past the excess R_3Al may have been needed to neutralize carboxylic acid in the starting neodymium carboxylate.[9]

This system also differed from those in the literature in that varying the R_3 in the R_3Al initiator from the usual $^iBu_3$ and $^iBu_2H$ to Me_3 and Et_3 caused no significant difference in the polymerization. In the past, Me_3Al has not been as effective.[10,17] Another feature of this system is that no effect was observed in varying the metal from Nd to La. Since these metals are of similar size, it is reasonable that they can have similar chemistry.[22] However, Nd has usually been the favored metal in the past.[10−19,23−29]

Comparison of the ternary system above with a binary isoprene polymerization system using just the lanthanide tris-2,2-dimethylbutyrates, $\{Ln[O_2CC(Me)_2Et]_3\}_x$, and R_3Al initiators provided the first chance to compare ternary and binary catalysts which start with the same fully characterized precursors. In the past, the binary systems typically used base adducts of $NdCl_3$ (for example, the phosphate complex $NdCl_3$(tributylphosphate)$_3$[11]) which were compared with carboxylates. The systems compared here allow a clear evaluation of the importance of chloride when other factors are kept constant.

The results in Table 1 show that there is a significant chloride effect in this well-controlled system. The binary system is like the ternary system in that the nature of the metal, La or Nd, and the nature of the R_3Al initiator do not affect the results significantly. In addition, large excesses of R_3Al initiator are not needed in the binary system. However, in the absence of chloride in the binary system, a soluble polyisoprene product is obtained which has a bimodal distribution of polymers and contains both *cis*- and *trans*-1,4-polyisoprene. This may prove to be of interest as a method to generate polymer blends in situ.

It is interesting to note that the simpler binary system is the one that provides the bimodal distributions. Bimodal distributions are usually thought to arise due to the presence of more than one catalytic site. It is more likely that multiple initiation sites would arise from the more complicated ternary system.

These results are consistent with the traditional view that chloride is an essential component of the catalyst which forms *cis*-1,4-polyisoprene. In the absence of chloride, the cis isomer can also form, but polymerization to *trans*-1,4-polyisoprene also occurs to generate a blend of isomers.

Conclusion

This study shows the importance of chloride in selectively forming high *cis*-1,4-polyisoprene in a comparison of equivalent binary and ternary lanthanide systems starting with fully characterized carboxylates. With these starting materials, both La and Nd are successful, and a variety of R_3Al activators can be used.

Experimental Section

General. Procedures were conducted under nitrogen using glovebox and Schlenk techniques except when the polymers were processed and washed. $\{Nd[O_2CC(Me)_2Et]_3\}_x$, **1**, and $\{La[O_2CC(Me)_2Et]_3\}_x$, **2**, were synthesized as previously described.[7] Et_2AlCl, $AlMe_3$, $AlEt_3$, AlH^iBu_2, and Al^iBu_3 (1.0 M solution in hexane) were purchased from Aldrich and used without further purification. Hexane was saturated with UHP grade argon and dried by passage through drying columns by GlassContour (Irvine, CA). Isoprene was purchased from Aldrich, dried over $MgSO_4$, and distilled before use. Gel permeation chromatography (GPC) data were obtained with THF solutions using a Waters 600 pump, three 30 cm columns (HR 4E, HR 5E, Euragel HE 145), and a Waters 410 refractometer detector. Column temperature and flow rate were 45 °C and 1 mL/min. The system was calibrated with standard polystyrenes. ^{13}C NMR spectra of the polymers were obtained on Omega 500 MHz and GN 500 MHz NMR spectrometers at 25 °C.

The Ternary Catalytic System. **1** (3.2 g, 6.5 mmol) was suspended in 5 mL of hexane, and Et_2AlCl (16.3 mL of a 1.0 M solution, 16.3 mmol) was added via syringe. The solution was stirred for 1 h at room temperature and filtered through a course filter frit. The solids were washed three times with 20 mL of hexane, to remove diethylaluminum carboxylate, and dried by rotary evaporation to yield a light blue powder for neodymium (2.0 g). A portion of this product (0.02 g, 0.03 mmol of Nd based on elemental analysis) was placed in a 20 mL vial, and AlR_3 (0.03 mL of a 1.0 M solution, 0.03 mmol) was added to the suspension. The mixture was stirred for 10 min, after which time isoprene (3 mL, 30 mmol) was added. After the suspension was stirred for an hour at room temperature, a plug of polymer had formed. Evaporation of the hexanes left an elastomer. The elastomer was quenched with 0.1% BHT in 2-propanol and 1 mL of 5% hydrochloric acid.

Similarly, **2** (6.2 g, 12.8 mmol) was treated with Et_2AlCl (32.0 mL of a 1.0 M solution, 32.0 mmol) to form a white powder (3.1 g). A 0.02 g portion of the lanthanum product (0.03 mmol of La) was used to polymerize isoprene as discussed for Nd.

The Binary Catalytic System. In a nitrogen-containing glovebox, AlR_3 (0.12 mL of a 1.0 M solution, 0.12 mmol) was added to a 20 mL vial containing $\{Nd[O_2C(Me)_2Et]_3\}_x$, **1** (0.02 g, 0.04 mmol), or $\{La[O_2C(Me)_2Et]_3\}_x$, **2** (0.02 g, 0.04 mmol), in 5 mL of hexanes. The mixture was stirred for 10 min, after which time isoprene (3 mL, 30 mmol), was added to the mixture. The suspension was stirred overnight to form a thick, light yellow solution in the lanthanum cases and a thick, light green solution in the neodymium reactions. The hexanes were evaporated to give an elastomer which was quenched with 0.1% BHT in 2-propanol and washed with 1 mL of 5% hydrochloric acid.

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