polymerization, and the mixture was stirred overnight at room temperature.
(26) Ten molar equivalents of 1,2-epoxypropane with respect to aluminum porphyrin was added to the copolymerization system after the first stage of the copolymerization, and the mixture was stirred overnight at room temperature, followed by evacuating the reaction system to remove 1,2-epoxypropane that remained unreacted.

Recyclable Polymer-Bound Lanthanide Diene Polymerization Catalysts

David E. Bergbreiter,* Li-Ban Chen, and Rama Chandran

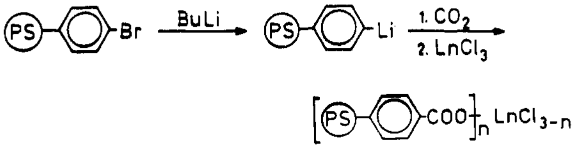
Department of Chemistry, Texas A&M University, College Station, Texas 77843.
Received November 26, 1984

ABSTRACT: Divinylbenzene cross-linked polystyrene bound neodymium and cerium catalysts that polymerize butadiene stereospecifically to form *cis*-1,4-polybutadiene in the presence of organoaluminum reagents are described. These immobilized catalysts can be recycled without significant loss of activity or selectivity. Neodymium chloride was also attached to carboxylated polyethylene to form a polyethylene-bound neodymium carboxylate that formed a homogeneous diene polymerization catalyst in solutions of aromatic solvents in the presence of triethylaluminum and ethylaluminum dichloride. Polybutadiene was successfully separated from the precipitated polyethylene-bound catalyst at room temperature after dilution of the reaction mixture with additional solvent but the activity of these polyethylene-entrapped catalysts was not significantly better than the activity of the polystyrene-bound catalysts.

Lanthanide salts in the presence of organoaluminum reagents are known to be useful as catalysts in stereospecific polymerizations of butadiene and isoprene.[1-4] Generally these catalysts are used in the form of suspensions in hydrocarbon solvents although homogeneous polymerizations can be carried out with lanthanide carboxylates instead of lanthanide halides as catalyst precursors.[5] These catalysts have not proven to be reusable. In this paper, we describe our initial efforts to develop recyclable lanthanide diene polymerization catalysts which have led to the preparation of reusable polymer-bound catalysts for these polymerization reactions.

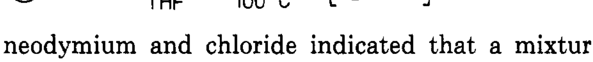
Although polymer-supported catalysts have seen widespread use in other reactions,[6,7] there are fewer examples of polymer-supported diene polymerization catalysts. Ziegler-type catalysts for diene polymerization have been anchored onto polymers,[8] but there are no reports in which lanthanide catalysts have been used in this fashion. In order to develop recyclable lanthanide polymerization catalysts, we had to first bind such catalysts to a suitable insoluble polymer. Since several sorts of insoluble carboxylated polymers are readily available and since lanthanide carboxylates were reported to function as useful lanthanide diene polymerization catalyst precursors, our initial studies focused on polymeric carboxylate salts of cerium and neodymium. The studies reported in this paper describe polystyrene-bound and polyethylene-bound carboxylate salts of neodymium and their use in diene polymerization.

Carboxylated DVB-cross-linked polystyrene (2% divinylbenzene cross-linking) was obtained by literature procedures[9] and exchanged with either neodymium chloride or cerium chloride (eq 1). The resulting resins mainly contained $Nd(O_2C\text{–}PS)_3$ and $Ce(O_2C\text{–}PS)_3$, which had Nd and Ce loadings of 0.86 and 1.19 mmol of Nd and Ce/g of polymer, respectively, as determined by combustion of these polymers and analysis of the ash. Each of these polystyrene-bound lanthanide carboxylates contained some residual chloride based on analysis for halogen using a Volhard titration. The chloride content of the Nd resin was 0.3% and the Ce resin contained 0.34% chloride (0.08 and 0.10 mmol of Cl/g of polymer, respectively). We presume that the exchange process by which the lanthanide salts are incorporated into the polystyrene did not result in quantitative exchange of chloride from the lanthanide precursor. Such a result is perhaps expected because of the increasing amount of cross-linking that occurs as the resin-bound carboxylates displace chloride from the lanthanide metal. We were unable to ascertain from IR spectroscopy if small amounts of $PS\text{–}CO_2Li$ remained unreacted in any of these catalyst precursors. However, flame tests of these polymers failed to detect lithium.



(1)

Neodymium derivatives of carboxylated polyethylene were obtained from commercially available oxidized polyethylene (0.5 mequiv of CO_2H/g of polymer) by the procedure of eq 2. Analysis of the resulting polymer for neodymium and chloride indicated that a mixture of neodymium chlorocarboxylates of average stoichiometry $(PE\text{–}CO_2)_{2.3}NdCl_{0.7}$ had formed. A band at 1710 cm^{-1} in the neodymium-containing polyethylene indicated either that some unreacted carboxylic acid groups or that other carbonyl groups remained in this polymer.[10]



$$\text{PE–COOH} \xrightarrow[\text{THF}]{R_2NLi} \xrightarrow[100\ °C]{NdCl_3} [\text{PE–COO}]_n NdCl_{3-n} \qquad (2)$$

Polymerizations of dienes were carried out by first forming the catalyst and then adding the diene to be polymerized. In a typical procedure, 0.02 g of the neodymium-containing carboxylated polystyrene resin (0.017 mmol of Nd) and 1.7 mL of a benzene solution that was 0.41 M in i-Bu_3Al and 0.22 M in $AlEt_2Cl$ were added to a 20-mL glass tube and allowed to stand at room temperature for 3 h. Then 4.8 mL of butadiene in benzene (0.15 g of C_4H_6/mL) was added and the glass tube was sealed. The reactions were allowed to stir using a magnetic stirring bar for 2 days. Workup consisted of addition of 10 mL of additional dry benzene to dilute the viscous reaction solution followed by centrifugation and forced

0024-9297/85/2218-1055$01.50/0

Table I
Diene Polymerization Using Lanthanide Laurates and Polystyrene Carboxylates[a]

catalyst	cocatalyst[b]	solvent	Ln/ diene, mol/g	temp, °C	time, h	conv,[c] %	microstructure,[d] %			[η], dL/g
							1.4-cis	1,4-trans	1,2	
$(C_{11}H_{23}CO_2)_3Nd$	A	C_6H_6	6.2	70	36	29	67	25	8	0.016
$(C_{11}H_{23}CO_2)_3Nd$	B	C_6H_{12}	6.2	70	36	56	96	3	1	6.4
$Ce(O_2C\text{–}PS)_3$[e]	B	C_6H_{12}	5.9	70	36	8	97	1	2	*f*
$Ce(O_2C\text{–}PS)_3$[e]	B	C_6H_{12}	52.6	70	36	53	95	3	2	*f*
$Ce(O_2C\text{–}PS)_3$ (1)[g]	B	C_6H_6	32	70	48	38	91	5	4	*f*
$Ce(O_2C\text{–}PS)_3$ (4)[g]	B	C_6H_6	24	70	48	5	97	2	1	*f*
$Ce(O_2C\text{–}PS)_3$ (1)[g]	B	C_6H_6	49	70	48	46	96	3	1	*f*
$Ce(O_2C\text{–}PS)_3$ (2)[g]	B	C_6H_6	70	70	48	26	95	3	2	*f*
$Nd(O_2C\text{–}PS)_3$ (2)[g]	B	C_6H_6	25	70	48	44	96	2	2	3.2
$Nd(O_2C\text{–}PS)_3$ (3)[g]	B	C_6H_6	25	70	48	38	97	2	1	4.8
$Nd(O_2C\text{–}PS)_3$ (4)[g]	B	C_6H_6	25	70	48	31	97	2	1	1.6
$Nd(O_2C\text{–}PS)_3$ (1)[g]	A	C_6H_6	25	70	48	100	68	28	4	0.013
$Nd(O_2C\text{–}PS)_3$ (2)[g]	A	C_6H_6	25	70	48	92	73	22	5	*f*
$Nd(O_2C\text{–}PE)_{2.5}Cl_{0.7}$ (1)[g]	B	C_7H_8[h]	100	100	10	25	93	4	3	*f*
$Nd(O_2C\text{–}PE)_{2.3}Cl_{0.7}$ (2)[g]	B	C_7H_8[h]	100	100	10	18	90	7	3	*f*

[a] Polymerizations were carried out by procedures described in the text. [b] Cocatalyst A was $Al_2Me_3Cl_3$; cocatalyst B was a mixture of $i\text{-}Bu_3Al$ and $AlEt_2Cl$. Cocatalyst A was present in a molar ratio of 40/1 relative to the Ln ion. Cocatalyst B was usually present in a $i\text{-}Bu_3Al/AlEt_2Cl/Ln$ molar ratio of 40/2/1. Small changes in these ratios of cocatalyst to Ln did not significantly affect our results. [c] Conversion is defined as the grams of polymer formed per gram of diene starting material. [d] The polymer's microstructure was determined by the procedures used in ref 1. [e] This catalyst was not recyclable in hexane. [f] Value not determined. [g] The number in parentheses refers to the number of times the catalyst in question was recycled before the polymerization data listed were determined.

siphoning of the polybutadiene solution away from the catalyst resin. Polybutadiene was then precipitated from solution by addition of ethanol. The catalyst resin was washed with 5 mL of dry benzene at which point it was ready for a second polymerization reaction.

Recycling of the catalyst resin had to be carried out under anhydrous, oxygen-free conditions. Recycling of the catalyst was also complicated by other experimental difficulties. First, centrifugation was only successful at separating the catalyst resin when the viscous polymer solutions were diluted with added benzene solvent. Second, the presence of polybutadiene gel polymer in some cases coated the polystyrene resin, rendering the recovered lanthanide catalysts inactive in further polymerizations. This problem was particularly troublesome when hexane was used as a solvent for the polymerization. Conversions of butadiene to polybutadiene generally decreased slightly in successive reactions even when benzene was used as a solvent for the polymerization. This may also be due to fouling of the catalyst resin with gel. The 25% lower conversion after several cycles also was due in part to physical loss of catalyst resin during the forced siphon of the supernatant polybutadiene solution from the catalyst residue.

Representative examples of the results of these experiments are detailed in Table I. Results of a comparable copolymerization using neodymium laurate in homogeneous solution are also included for comparison purposes. In some of these experiments, $Al_2Me_3Cl_3$ was used in place of $i\text{-}Bu_3Al/AlEt_2Cl$ as a cocatalyst. In such cases, the polymerizations produced only low molecular weight oligomers of butadiene, which were recovered as liquids rather than as solids and which had a lower cis-1,4 microstructure.

Polymerizations of butadiene using the polyethylene-bound neodymium catalyst were carried out by procedures similar to those used with the polystyrene-bound catalysts with the expectation that lanthanide catalysts attached to functionalized ethylene oligomers could be used as homogeneous catalysts yet recovered as polyethylene dispersions.[11] However, although the polyethylene-bound catalysts were homogeneous at sufficiently high temperatures (ca. 110 °C), no dramatic increases in catalytic activity were seen. Under the typical reaction conditions employed (100 °C), a small amount of the polyethylene-bound catalyst was present in the form of a solvent-swollen polymer gel. Comparison of reactions of the polystyrene-bound neodymium catalyst and the polyethylene-bound neodymium catalysts shows that the polyethylene-bound catalyst was not significantly better than the polystyrene-bound catalyst. The conversions seen with the polystyrene-bound catalyst are perhaps slightly better than those seen with the polyethylene-bound catalyst considering the differences in polymerization temperature and time.

In summary, attachment of lanthanide metals to insoluble cross-linked polystyrene resins or to polyethylene via carboxylate groups leads to recyclable diene polymerization catalysts that possess the same sorts of stereoselectivity for formation of high molecular weight diene polymers seen in other diene polymerization catalysts. The activity of these polymer-bound catalysts varies but is comparable to that of typical lanthanide catalyst systems. The molecular weight of the product polybutadiene obtained from these polymers also varied significantly when other organoaluminum cocatalysts were used.

Experimental Section

General Procedures. Commercial butadiene was purchased from Matheson Co. and was purified by passing it through three successive columns that contained drying agent ($CaSO_4$), KOH, and molecular sieves, respectively. Hydrocarbon solvents were dried and deoxygenated by distillation from a solution or suspension of sodium–benzophenone. Organoaluminum reagents were commercial products obtained from Aldrich Chemical Co. Macroreticular polystyrene, brominated polystyrene, and oxidized polyethylene were all obtained from Aldrich Chemical Co. and were purified prior to use either by extraction with toluene in a Soxhlet for 1 day (polystyrene polymers) or by dissolution in hot toluene followed by precipitation on cooling. Characterization of both the polymeric catalysts and the polybutadiene products was accomplished by IR analysis using an SP3-200 spectrophotometer. The relative amounts of *cis*-1,4-, 1,2-, and *trans*-1,4-polybutadiene were determined by measuring the corresponding optical density D_ν at ν = 738, 911, and 967 cm^{-1}, respectively. The intrinsic viscosity of these polymers was determined with an Ubbelohde viscosimeter in toluene solutions at 30 °C.

Polystyrene-Bound Lanthanide Carboxylates. Brominated polystyrene (5 g, 4.36 mmol of Br/g) was swollen in 100 mL of dry toluene, and 38 mL of 1.52 M *n*-butyllithium in hexane was added with a syringe. The resulting suspension was stirred at 90 °C overnight. The liquid phase was then removed by forced siphon through a cannula, and the resin was washed several times with dry THF to remove any soluble impurities. Carboxylation of the lithiated polystyrene was accomplished by addition of a slurry of dry ice in THF. After several hours, the resulting carboxylated resin was washed first with THF/water, then with THF, and finally with methanol and dried. An IR spectrum of the resulting PS-COOLi (KBr pellet) had a carbonyl absorption at 1550 cm^{-1}. Washing this PS-COOLi resin with a 1.32 N HCl/THF solution and then with THF/H_2O and methanol and finally drying the resulting resin produced PS-COOH, which had a peak at 1710 cm^{-1} in the IR (KBr pellet). Lanthanide carboxylates were prepared directly from PS-COOLi by reaction with $CeCl_3$ or $NdCl_3$. For example, 1 g of the PS-COOLi swollen in 5 mL of THF and a solution of 1.2324 g of $CeCl_3$ in 10 mL of H_2O was stirred at 70 °C for 1 h and at room temperature overnight. After removal of the liquid phase, the resin was washed successively with THF/water, THF, and finally methanol and then dried. A flame test indicated that the resin did not contain significant amounts of Li. The amount of cerium in the resin was determined by burning a small portion of the resin in a crucible to give 19.54% of an ash, which was cerium oxide. The balance of the initial amount of cerium was found in the combined washes.

Neodymium Dodecanoate. Neodymium dodecanoate was prepared from dodecanoic acid by first preparing an emulsion of 12 g of dodecanoic acid (60 mmol) in 400 mL of H_2O which was neutralized with a solution of 2.4 g of NaOH in 50 mL of H_2O. The clear solution of sodium dodecanoate that formed was then allowed to react with 6.6 g of $Nd(NO_3)_3 \cdot 5H_2O$ (20 mmol) in 50 mL of H_2O. A white precipitate formed, which was separated by centrifugation and then washed with H_2O and methanol several times. After 15 h of drying in vacuo at 110 °C, 9.7 g of $(C_{11}H_{23}CO_2)_3Nd$ was obtained (65%). A small portion of this product was analyzed by burning it and analyzing the ash for Nd_2O_3. Anal. Calcd for $(C_{11}H_{23}CO_2)_3Nd$: Nd, 19.43. Found: Nd, 19.92.

Polyethylene-Bound Neodymium Carboxylate. A solution of 2 g of oxidized polyethylene (density 0.99, 0.5 mequiv of CO_2H/g of polymer) was prepared in 40 mL of toluene at 100 °C. Addition of 2.0 mequiv of lithium diisopropylamide by syringe rapidly formed a gel. Addition of 0.6 g (1.5 mequiv) of $NdCl_3(THF)_2$ as a suspension in 10 mL THF produced a suspension, which was stirred for 8 h at 100 °C. After cooling, the resulting polymer precipitate was isolated by centrifugation and then washed several times with methanol. After drying in vacuo at 60 °C overnight, the final product was isolated and found to have a broad peak at 1540–1560 cm^{-1} along with a carbonyl peak of reduced intensity at 1710 cm^{-1}. The product polymer was next placed in a jacketed Soxhlet extraction apparatus and extracted with hot toluene to remove the desired toluene-soluble product from any inadvertently formed insoluble neodymium byproducts. Analysis as above for neodymium showed that this polymer contained 3.2% Nd and 0.5% Cl.

Polymerization of Butadiene Using Polystyrene-Bound Catalysts. In a typical experiment, 0.0202 g of $Nd(O_2C\text{-}PS)_3$ (0.017 mmol of Nd) was added to 1.7 mL of a benzene solution that was 0.41 M in triisobutylaluminum and 0.022 M in diethylaluminum chloride. After this catalyst mixture was allowed to stand at room temperature for 3 h, 4.8 mL of a benzene solution of butadiene that contained 0.147 g of butadiene/mL of solution was added. The reaction vessel was then sealed with a glass stopper attached to a short piece of rubber tubing and heating with stirring at 70 °C for 2 days. Before the reaction was worked up, 10 mL of additional benzene was added to dilute the reaction solution. After cooling, the solution was separated from the catalyst resin by centrifugation and transferred by syringe into a beaker. The product polybutadiene was then precipitated from solution by addition of ethanol and characterized as described previously.[1] For recycling, the catalyst was washed with 5 mL of dry benzene before use in the next polymerization cycle. Subsequent cycles required additional alkylaluminum cocatalyst.

Butadiene Polymerization Using Polyethylene-Bound Neodymium Carboxylate. To a suspension of 0.2 g of polyethylene-bound neodymium carboxylate in 20 mL of benzene was added 1.5 mL of a benzene solution of a mixture of triethylaluminum and diethylaluminum chloride (40:1, mmol:mmol). A solution of 3.4 g of butadiene in 7 mL of benzene was then added to this suspension of catalyst and cocatalyst and the reaction mixture was sealed in a pressure vessel. After heating and stirring for 10 h at 100 °C, the reaction was cooled and diluted with additional benzene to reduce the viscosity of the product mixture. Centrifugation separated the insoluble polyethylene from the benzene solution of polybutadiene. The product polybutadiene was recovered as described above and characterized by IR as previously described. The recovered polymer was recycled after two benzene washes. In the presence of added alkylaluminum reagents, the same polymer was about as active as it was originally. However, without addition of more cocatalyst no activity was seen.

Acknowledgment. Support of this research by the Texas A&M Center for Energy and Mineral Resources and by the Petroleum Research Fund is gratefully acknowledged.

References and Notes

(1) Yang, J.-H.; Tsutsui, M.; Chen. Z.; Bergbreiter, D. E. *Macromolecules* **1982**, *15*, 230–233.

(2) Shen, Z.; Ouyang, J.; Wang, F.; Hu, Z.; Yu, F.; Qian, B. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3345–3354. Shen, Z.; Song, X.; Xiao, S.; Yang, J.; Kan, X. *J. Appl. Polym. Sci.* **1983**, *28*, 1585–1597.

(3) For examples of actinide catalysts, cf.: Lugli, G.; Mazzei, A.; Poggio, S. *Makromol. Chem.* **1974**, *175*, 2021–2027.

(4) Boor, J., Jr. "Ziegler–Natta Catalysts and Polymerizations"; Academic Press: New York, 1979.

(5) Sylvester, G.; Witte, J.; Marwede, G. Ger. Offen. 2848964, 1980; *Chem. Abstr.* **1981**, *93*, 96555*d*.

(6) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109–148.

(7) Chauvin, Y.; Commereuc, D.; Dawans, F. *Prog. Polym. Sci* **1977**, *5*, 95–226.

(8) Dawans, F.; Morel, D. *J. Mol. Catal.* **1978**, *3*, 403–415.

(9) Farrall, M. J.; Frechet, J. M. J. *J. Org. Chem.* **1976**, *41*, 3877–3882.

(10) Nuzzo, R. G.; Smolinsky, G. *Macromolecules* **1984**, *17*, 1013–1019.

(11) Bergbreiter, D. E.; Chen, Z.; Hu, H.-P. *Macromolecules* **1984**, *17*, 2111–2116.