A rare earth catalyst for diene polymerization based on butyl lithium

D. K. Jenkins

EniChem Elastomers Ltd, Charleston Road, Hardley, Hythe, Southampton, SO4 6YY, UK

(Received 5 October 1990; revised 4 January 1991; accepted 16 January 1991)

Butyl lithium can be used in place of aluminium alkyls in catalysts of the AlR_3/neodymium complex/Al alkyl halide type. With catalysts consisting of Al alkyl halide/neodymium complex/BuLi, both order of addition and, in particular, the ratio of catalyst components are critical. Polymer with a high *cis* content can be made from butadiene and isoprene but conversions are lower and more variable than with standard aluminium alkyl-based catalysts, even when high catalyst concentrations are used. The catalyst can be used as a premix or added to mixed feed as separate components. In both cases the catalyst mixture is somewhat heterogeneous and polymerization rates are improved by shaking or stirring during polymerization.

(Keywords: butyl lithium; neodymium; butadiene; isoprene; high *cis*; aluminium alkyl halide)

INTRODUCTION

Neodymium-based catalysts, for solution polymerization of dienes to high-*cis* polymer, can be divided into two types, depending on the source of halide. Most systems are based on $AlBu_3$ or $AlBu_2H$ and Nd complexes, but one group of catalysts has aluminium trihalide, aluminium alkyl halide or alkyl halide as a separate third component[1–5], while the other has only two components and the halide is present in the form of various $NdCl_3$ complexes[6–12].

It has been discovered that a combination of $MgBu_2$ and soluble neodymium carboxylate polymerizes butadiene (Bd) to high-*trans* polymer[13]. By combining this catalyst with the correct amount of aluminium alkyl halide, a novel system was formed which gave high-*cis* polybutadiene[14]. Asahi adapted this catalyst[15] to produce a styrene/*trans* Bd diblock copolymer by polymerizing styrene with $MgBu_2$ and BuLi and adding Bd and a Nd complex to form the *trans* block. It has also been shown[13] that the rare earth/$MgBu_2$ catalyst can be modified by the addition of BuLi, such that with increasing Li:Nd ratio, the microstructure changes gradually from high *trans* to that associated with anionic polymerization by BuLi alone, i.e. approximately 50% *trans*, 40% *cis*, 10% vinyl. Although catalysts consisting of BuLi, $MgBu_2$ and barium compounds are known to give styrene butadiene rubber (SBR) polymers of 70% *trans* or more[16], it was not possible to establish conclusively whether the 70% *trans* Bd polymer, which could be made with BuLi, $MgBu_2$ and rare earth compounds, was a copolymer or a mixture of high and medium *trans* homopolymers. In the absence of $MgBu_2$, the combination of BuLi and rare earth compound gives poor yields of 50% *trans* polymer.

From the above information it could reasonably be concluded that a rare earth catalyst incorporating BuLi would be unlikely to produce a high-*cis* polymer. However, one theory of how the $MgBu_2$/Nd versatate (Nd neodecanoate)/$AlEt_2Cl$ mixture forms an active catalyst is that the $MgBu_2$ reacts with a slight excess of $AlEt_2Cl$ forming inactive $MgCl_2$ and leaving the correct amount of active chloride and alkyl groups for chlorination and alkylation of Nd. On this basis BuLi should react in a similar way to form LiCl, but with one less butyl group available for alkylation of Nd.

EXPERIMENTAL

Hexane (Fisons SLR grade, mixed isomers) was distilled from butyl lithium solution under dry nitrogen.

Butyl lithium was supplied by Lithco (UK) as a 15.1% w/w solution in hexane and was diluted in hexane as required.

Butadiene was distilled from a liquid, inhibited (tertiary butyl catechol) supply through one glass column containing KOH pellets and through three columns containing alumina (dried at 400°C). The vapour was condensed into bottles containing 75 ml hexane at -20 to -30°C to give approximately 14 g Bd per bottle. The actual quantity of Bd was found by weighing before and after distillation.

Isoprene (Aldrich) was treated with ethanolic KOH and acetone to remove inhibitor and cyclopentadiene. The mixture was washed with water, separated and the isoprene dried over alumina. The isoprene was finally distilled through an alumina-packed column and added to bottles with a syringe.

The aluminium compounds $AlBu_2H$, $Al_2Et_3Cl_3$ and $AlEt_2Cl$ (Aldrich) were used as received and diluted in hexane as required.

Neodymium versatate (NdV_3) was prepared from aqueous $NdCl_3$ by reaction with three equivalents of aqueous sodium versatate (versatic acid (Shell 'Versatic 10') plus aqueous NaOH). The product was extracted into hexane, purged with nitrogen and the solution analysed for Nd content by ethylenediamine tetracetic acid–zinc titration with dithizone indicator.

Solvents were transferred, under nitrogen pressure, via double-ended steel needles, and reagents and catalysts were added by syringe.

0032-3861/92/010156-05

Catalyst preparation and polymerizations were done in 260 ml crown-capped soda glass bottles, which had been kept at 120°C and flushed with dry nitrogen while cooling. Nitrile rubber seals, used under the metal caps, were Soxhlet extracted with heptane for 7 h to remove phthalate plasticizer, and finally dried under vacuum at 50°C.

Catalyst premixes were prepared at ~20°C by adding the appropriate quantity of $AlEt_2Cl$ to 100 ml of hexane in a bottle. The NdV_3 solution was added dropwise by syringe and after stirring for 45 min, BuLi in hexane solution was slowly added. Premixes were used after ageing at ambient temperature for 20 h, unless otherwise indicated. In all other cases the catalyst components were added separately to a diene/hexane mixed feed.

Bottle shaking was done in an LTE Unitemp thermostatted shaker water bath. The original spring bottle cage retainers were replaced by upright pillars welded to the shaker tray base.

Hexane/diene mixed feed was heated to 60°C in caged bottles in a water bath before adding catalyst. Polymerizations were run at 60°C in all cases.

After the desired time, bottles containing polymer cement were vented to release excess monomer. One per cent (on polymer) of a 5:1 mixture of Polygard and Irganox 565 antioxidants in hexane was added to the cement and, after mixing as far as possible, the polymer was coagulated in an excess of methanol.

For inherent viscosity (i.v.) measurements, wet polymer cement containing approximately 0.1 g polymer was dissolved in 100 ml of toluene. The accurate weight of polymer was subsequently found from the solids content of the filtered toluene solution. Measurements of i.v. were done at 30°C.

The remaining polymer was dried for 7 h at 50°C *in vacuo*. Approximately 0.03 g of the dried polymer was used for gel permeation chromatography (g.p.c.) measurements in tetrahydrofuran (THF) using a Du Pont 870 pump module gel permeation chromatograph with 860 column compartment, Shimadzu RID 6A refractometer and four Ultrastyragel columns.

Gel content was determined by dissolving 0.5 g of polymer in 100 ml toluene overnight, centrifuging approximately 35 ml of the mixture at 16000 rev min^{-1} for 2 h and determining the solids content of 20 ml of the supernatant. Percentage gel was calculated from the difference between the original weight of polymer and the amount dissolved.

RESULTS AND DISCUSSION

In initial experiments using Bd as monomer and adding the catalyst components separately to hexane/Bd mixed feed, part of the $AlBu_2H$ in a catalyst, normally used at a ratio of 20:1:3 $AlBu_2H$/Nd versatate/$AlEt_2Cl$, was replaced with increasing amounts of BuLi. The results showed that no polymer was formed with a *cis* content between high-*cis* in the absence of BuLi and the 40% expected from the use of BuLi alone.

In the light of these experiments, it was concluded that BuLi was probably reacting with the small amount of $AlEt_2Cl$ present to remove chloride completely as LiCl. Therefore, further experiments were done in which the ratio of $AlEt_2Cl$:BuLi was equal to or greater than 1:1 by using a BuLi:Nd ratio of 10:1 and increasing the level of $AlEt_2Cl$ (*Table 1*).

Table 1 Molar ratio and order of addition of catalyst components. Polymerization for 4.5 h. [Nd] = 0.13 mM per 100 g Bd

Ratio of $AlEt_2Cl:NdV_3:BuLi$	Conversion (%)	*Trans* (%)	*Cis* (%)	Vinyl (%)
10:1:10	1.2	–	–	–
12.5:1:10	2.3	–	–	–
[a]15:1:10	12.7	2.2	97.5	0.3
17.5:1:10	1.3	–	–	–
20:1:10	0.9	–	–	–

[a] I.v. = 3.4; MWD = 5.03

With [Nd] = 0.13 mM per 100 g Bd and Al:Li ratios of 1:1 to 1.5:1, soluble high-*cis* polymer was formed in low yield with maximum conversion at a ratio of 1.5:1. As the catalyst components were added, a cloudy yellowish suspension formed in the mixed feed. By contrast, at Al:Li ratios greater than 1.5:1, a whitish precipitate formed within a few minutes of catalyst formation and polymer was produced in very low yield as a gel at the bottom of the bottle, even when vigorously shaken. It was essential to add BuLi as the final component to get an active catalyst.

Further experiments were done (*Table 2*) to improve conversion and optimize catalyst levels and ratios.

Other aluminium alkyl halides were tried in the system, in place of $AlEt_2Cl$. Addition of $AlEtCl_2$ to mixed feed caused immediate precipitation of a small quantity of yellowish solid before the other components were added. At various catalyst ratios, less than 3% conversion was obtained and the polymer did not appear to have a high *cis* content. The initial precipitation was probably due to rapid cationic polymerization of Bd to insoluble polymer. With $Al_2Et_3Cl_3$ used at Cl:Nd:Li ratios between 22.5:1:20 and 27.5:1:20 with [Nd] = 0.13 mM per 100 g Bd and at 35:1:30 with [Nd] = 0.26 mM per 100 g Bd, the catalyst precipitated after the components were mixed, conversion to polymer was less than 3% and the product was a mixture of gel and high-*cis* polymer. In a further attempt to obtain a reasonable yield of polymer by increasing the $Al_2Et_3Cl_3$ and BuLi levels relative to Nd, the results shown in *Table 3* were obtained.

A comparison of shaken and unshaken polymerizations was made during experiments to determine the rate of polymerization (*Table 4*): in the early stages of polymerization the rate is approximately doubled by shaking.

Higher rates of conversion with the standard $AlBu_2H/NdV_3/AlEt_2Cl$ catalyst are obtained if the components are added separately to mixed feed rather than premixed in the absence of monomer but, in contrast, better results with an $AlBu_2H/NdV_3/{}^tBuCl$ catalyst are obtained by using an aged premix. Since BuLi and $AlEt_2Cl$ should react rapidly to form LiCl it was expected that premixing the BuLi-based catalyst would give a system of very low activity. However, as shown in *Table 5*, premixing in the absence of monomer and ageing for 20 h gave a catalyst of reasonable activity, although rate of polymerization was lower than with unmixed components.

G.p.c. traces for typical Bd polymerizations are shown in *Figure 1* for the BuLi based systems. In general the

Table 2 Ratios of catalyst components and concentrations used to improve conversion. Polymerization for 5 h at 60°C. Bottles not shaken

Ratio of $AlEt_2Cl:NdV_3:BuLi$	Catalyst level (mM per 100 g Bd)	Conversion (%)	I.v.	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	Peak $M_w \times 10^{-3}$	MWD	*Cis* (%)
15:1:10	0.13	6.1	–	–	–	–	–	–
20:1:20	0.13	1.1	–	–	–	–	–	–
23:1:20	0.13	1.2	–	–	–	–	–	–
25:1:20	0.13	53.9	5.26	924	98	1334 462	9.4	94.4
27:1:20	0.13	51.2	6.18	962	182	1197	5.3	97.7
30:1:20	0.13	0.9	–	–	–	–	–	–
35:1:30	0.13	2.5	–	–	–	–	–	–
15:1:10	0.26	28.1	2.91	438	80	1047 73	5.5	97.2
24:1:20	0.26	61.5	3.74	633	135	1035 197	4.7	95.4
25:1:20	0.26	64.3	–	–	–	–	–	–
26:1:20	0.26	46.8	3.53	389	81	905 60	4.8	96.4
27:1:20	0.26	7.3	–	–	–	–	–	–
28:1:20	0.26	3.5	–	–	–	–	–	–
29:1:20	0.26	2.5	–	–	–	–	–	–
30:1:20	0.26	2.2	–	–	–	–	–	–

Table 3 Comparison of $AlEt_2Cl$ and $Al_2Et_3Cl_3$. Polymerization at 60°C for 4.5 h. [Nd] = 0.26 mM per 100 g Bd

Ratio of Cl:Nd:Li	Conversion (%)	I.v.	*Trans* (%)	*Cis* (%)	Vinyl (%)
$AlEt_2Cl$ (control)					
37.5:1:30	16.8	3.75	9.4	89.4	1.2
40:1:30	40.7	3.94	8.6	90.9	0.5
42.5:1:30	5.6	2.85	2.3	97.3	0.4
$Al_2Et_3Cl_3$					
37.5:1:30	1.6	–	–	–	–
40:1:30	3.7	–	–	–	–
42.5:1:30	68.3	5,03	2.7	97.0	0.3

Table 4 Effect of shaking on rate of polymerization. $AlEt_2Cl:NdV_3:BuLi = 25:1:20$. [Nd] = 0.26 mM per 100 g Bd

Conditions	Time (min)	Conv. (%)	I.v.	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	Peak $M_w \times 10^{-3}$	MWD	*Cis* (%)
Unshaken	30	4.8	–	–	–	–	–	–
Unshaken	60	5.9	–	–	–	–	–	–
Unshaken	120	11.3	3.18	347	33	836 240	10.6	92.5
Unshaken	180	32.8	3.63	545	71	944 243	7.7	91.8
Unshaken	270	61.5	3.74	633	135	1035 107	4.7	95.4
Shaken	30	8.8	2.97	499	127	1259 98	3.9	98.7
Shaken	60	22.2	3.80	534	54	1122 85	9.9	97.6
Shaken	120	29.3	3.78	482	103	901 98	4.7	96.7
Shaken	180	57.7	3.73	496	96	412	5.1	96.0
Shaken	240	69.0	3.76	525	70	1084 227	7.6	95.0

Table 5 Al:Nd:Li = 25:1:20. Polymerization for 4.5 h at 60°C. Premixed catalyst components, aged for 20 h

[Nd] (mM per 100 g Bd)	Conv. (%)	I.v.	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	Peak $M_w \times 10^{-3}$	MWD	*Cis* (%)
0.26	41.6	4.29	561	66	1202 596	8.5	97.9
0.39	61.1	3.42	395	68	468	5.8	96.6

Table 6 Results obtained with THF added to mixed feed before catalyst components. Polymerization for 4.5 h. [Nd] = 0.26 mM per100 g Bd

Ratio THF:Al:Nd:Li	Conv. (%)	I.v.	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	Peak $M_w \times 10^{-3}$	MWD	*Cis* (%)
0:25:1:20	62.7	3.61	526	82	1010 82	6.4	96.3
0.5:25:1:20	65.5	4.12	623	113	1059 676	5.5	96.6
0.75:25:1:20	20.8	5.34	–	–	–	–	99.1
1:25:1:20	2.5	–	–	–	–	–	–
3:25:1:20	0	–	–	–	–	–	–

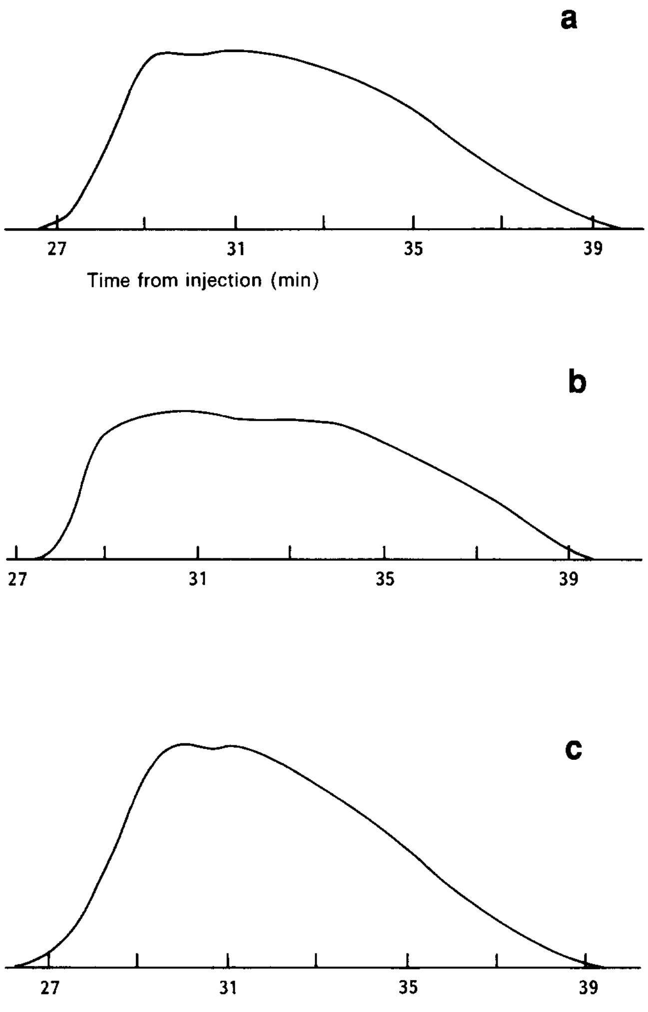

Figure 1 Gel permeation chromatography traces for typical polymerizations. (a) Butadiene monomer, catalyst components added separately. Conversion = 81.9%, $M_w = 581 \times 10^{-3}$, $M_n = 91 \times 10^{-3}$, MWD = 6.4. (b) Butadiene monomer, premixed catalyst. Conversion = 61.1%, $M_w = 596 \times 10^{-3}$, $M_n = 68 \times 10^{-3}$, MWD = 5.8. (c) Isoprene monomer, catalyst components added separately. Conversion = 56.1%, $M_w = 638 \times 10^{-3}$, $M_n = 135 \times 10^{-3}$, MWD = 4.7

polymer molecular weight distribution (MWD) tended towards bimodality even at full conversion. Since the catalysts appear to be somewhat heterogeneous, the bimodality may be due to formation of high molecular weight polymer on the insoluble fraction of the catalyst and lower molecular weight polymer by the soluble fraction. The gel content of polymer prepared under optimum conditions was about 3–4%.

The high-*trans* catalyst, $MgBu_2$ + Nd versatate, is activated by small amounts of THF[13]. Addition of THF to the corresponding high-*cis* catalyst[14] $AlEt_2Cl/NdV_3/MgBu_2$, initially causes a reduction in rate of polymerization and finally a switch to polymer with a high *trans* structure, presumably because $AlEt_2Cl$ becomes complexed by THF.THF added to the $AlEt_2Cl/NdV_3/BuLi$ catalyst (*Table 6*) caused a steady decrease in activity whilst a high-*cis* structure was maintained in the polymer. This would be consistent with the previous data for the magnesium alkyl-based catalysts, since NdV_3 + BuLi does not act as a *trans* polymerization catalyst and therefore removal of $AlEt_2Cl$ as a THF complex should have no effect on microstructure.

The experiments reported so far used Bd as monomer. Results in the literature suggest that rare earth catalysts, in general, polymerize isoprene at a slower rate than Bd. This is also the case for the BuLi-based catalysts as shown in *Table 7* and *Figure 2* where isoprene was used as monomer and a 25:1:20 molar ratio of $AlEt_2Cl:NdV_3:BuLi$ was assumed to be the optimum.

CONCLUSIONS

The overall conclusions are that the $AlEt_2Cl$ and $Al_2Et_3Cl_3$/Nd versatate/BuLi systems can be used successfully to polymerize both butadiene and isoprene to high-*cis* polymer in moderately high yield. A higher level of neodymium is required to obtain conversions comparable to known catalysts in which aluminium alkyls are used as alkylating components. The ratio of components and addition order required for optimum activity is critical and there is some variation in

Table 7 Polymerization rates using isoprene as monomer. Polymerization at 60°C in shaker bath. [Nd] = 0.26 mM per 100 g isoprene

Time (min)	Conv. (%)	I.v.	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	Peak $M_w \times 10^{-3}$	MWD	*Cis* (%)
30	15.5	2.83	–	–	–	–	–
60	18.4	3.20	776	168	1175	4.6	93.5
					692		
90	18.3	3.61	–	–	–	–	–
120	27.1	3.35	–	–	–	–	–
180	28.2	3.44	–	–	–	–	–
300	56.1	3.66	638	135	881	4.7	93.3
					155		

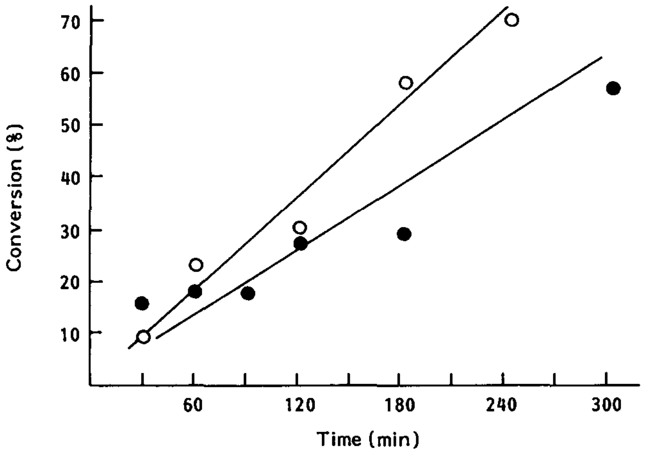

Figure 2 Comparison of rate of polymerization with butadiene (○) and isoprene (●) monomer. $AlEt_2Cl:NdV_3:BuLi$ = 25:1:20. Polymerization at 60°C. [Nd] = 0.26 mM per100 g monomer

conversion, in similar experiments, which may be due to the slightly heterogeneous nature of the active catalysts. It may be postulated that at the optimum ratio, BuLi reacts with $AlEt_2Cl$ to form a new alkyl component $AlEt_2Bu$, plus LiCl, leaving a small excess of $AlEt_2Cl$ to provide chlorination of neodymium. Formation of LiCl would account for the cloudiness of the catalyst solutions and the ratio of residual $AlEt_2Cl$:Nd would be close to the Cl:Nd ratio of 3:1 which seems to be the optimum for other rare earth-based catalysts.

ACKNOWLEDGEMENTS

Thanks are due to Mr R. Porter for g.p.c. analysis and to EniChem for permission to publish this work.

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