Butadiene polymerization with a rare earth compound using a magnesium alkyl cocatalyst: 2

D. K. Jenkins

EniChem Elastomers Ltd., Charleston Road, Hardley, Hythe, Southampton, SO4 6YY, UK
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A catalyst was developed for the preparation of high *cis* polybutadiene consisting of 'didymium' versatate – aluminium alkyl halide – magnesium dialkyl. By altering the order of component addition and using neodymium versatate, the catalyst activity and *cis* content of the polymer were both increased. The aluminium alkyl halide could be replaced by mixtures of aluminium trialkyl plus silicon halides or organic halides. Various additives were tried in order to reduce polymer molecular weight and to alter the molecular weight distribution.

INTRODUCTION

The first use of rare earth catalysts for high *cis* polybutadiene was published in 1963[1] by Von Dohlen. In the following year Chinese work was reported[2], which has been extended continuously to the present day and includes polymerization of isoprene[3], acetylene[4] and the use of different cocatalysts. A rare earth catalyst has also been used to polymerize 2,4-hexadiene[5], although in this case mainly *trans* units were formed. The original Chinese two component catalyst consisting of rare earth trichlorides and aluminium trialkyl was improved by Throckmorton[6] who used two and three component catalysts based on cerium. Much of the more recent work seems to stem from the very high (up to 99%) *cis* contents obtained in butadiene polymerization using uranium allyl catalysts[7]. The problem of radioactivity in these systems led to a reinvestigation of the rare earths. A useful chronological list of rare earth catalyst references prior to 1980 was given by Bruzzone[8]. Mazzei[9] and Witte[10] reported very similar catalysts involving rare earth alkoxides or carboxylates, in conjunction with aluminium alkyls and aluminium alkyl halides, which produced polybutadienes of 98–99% *cis* content in high yield at economic catalyst levels. Chinese work[11] on the whole range of rare earths has shown that high catalyst activity is confined to the consecutive elements cerium, neodymium and praseodymium and to gadolinium. Most current catalysts of commercial value are based on neodymium for reasons of activity and economy.

As discussed in Part 1 of this series of papers[12], initial experiments showed that a rare earth versatate-MgBu$_2$ catalyst modified with Al$_2$Et$_3$Cl$_3$ could be used to obtain high *cis* polybutadiene. This paper is concerned with the properties and development of that catalyst.

EXPERIMENTAL

The main experimental details were reported in Part 1[12]. Neodymium versatate was prepared from hydrated neo-

dymium chloride by the method used for 'didymium' versatate. After drying the solid versatate *in vacuo*, it was extracted with hexane to form an 0.2 M hazy, viscous solution. After a few days a white precipitate had formed, the solution viscosity had dropped considerably and the neodymium concentration was 0.18 M. A sample of this solution, after filtration, was diluted in hexane and used in the present work.

Silicon halides were purified by distillation. Organic halides were dried over fresh calcium oxide, redistilled under dry nitrogen and stored over 3 Å molecular sieves. Other additives for molecular weight control were dried and purified by standard methods.

Viscosity average molecular weights were calculated from intrinsic viscosities using the Mark–Houwink equation with $K = 3.24 \times 10^{-4}$ and $\alpha = 0.7$ for the high *cis* polymers[11]. Intrinsic viscosities (I.V.s) were carried out on 0.1% solutions of polymer in toluene at 30°C.

RESULTS AND DISCUSSION

By adding increasing amounts of aluminium ethyl sesquichloride, to a standard *trans* polymerization catalyst consisting of didymium versatate and magnesium dibutyl it was possible to change gradually from a *trans* microstructure to *cis*. Unfortunately the intermediate stages were of no practical use as conversions were very low. Conversion to *cis* polymer was >90% using the levels of rare earth required for satisfactory *trans* polymerization, with Didym:Mg:Al ratios of 0.1:1:1.

The first experiments were carried out with the three catalyst components added to butadiene in hexane solution in the order indicated above, i.e. rare earth compound first. Since the versatates seemed relatively inert and unlikely to react with butadiene or system impurities, this order of addition was retained for several sets of experiments. However, it was later found that by adding the aluminium alkyl halide before the rare earth compound, a considerable increase in activity could be

Table 1 Miscellaneous experiments

Order of Addition	Ratio	Time	Cat Level mM Nd/100g	Conv. %	Trans %	Cis %	Vinyl %
Didym : Mg : Al$_2$Et$_3$Cl$_3$	0.1 : 1 : 0.2	16 h	0.26	45.8	96.9	1.2	1.9
″ ″ ″	0.1 : 1 : 0.4	″	″	13.7	81.2	16.4	2.4
″ ″ ″	0.1 : 1 : 0.8	″	″	32.9	14.3	84.4	1.3
″ ″ ″	0.1 : 1 : 1.0	″	″	87.6	9.0	90.4	0.6
″ ″ ″	0.1 : 1 : 1.5	″	″	96.3	6.0	93.1	0.9
Nd : Mg : AlEtCl$_2$	0.1 : 1 : 0.75	16 h	0.26	98.3	4.7	94.7	0.6
AlEtCl$_2$: Nd : Mg	0.75 : 0.1 : 1	″	″	99.1	3.4	96.1	0.5
Didym : Mg : AlEt$_2$Cl	0.1 : 1 : 1.5	45 min	0.09	1.4	1.6	97.9	0.5
AlEt$_2$Cl : Didym : Mg	1.5 : 0.1 : 1.0	″	″	33.8	1.8	97.7	0.5
Nd : Mg : AlEt$_2$Cl	0.1 : 1 : 1.5	″	″	26.5	1.7	97.8	0.5
AlEt$_2$Cl : Nd : Mg	1.5 : 0.1 : 1.0	″	″	78.9	1.5	98.1	0.4

Temperature = 50°C

Table 2 Effect of catalyst concentration

Concentration mM Nd/100g Bd	Temperature (°C)	% Conversion	Intrinsic viscosity	Trans	Cis	Vinyl
0.26	50°	100	5.8	3.6	96.1	0.3
0.13	″	97.1	6.1	1.6	98.0	0.4
0.09	″	97.8	7.8	1.3	98.4	0.3
0.07	″	98.3	6.7	2.0	97.5	0.5
0.05	″	99.4	7.0	1.5	98.0	0.5
0.04	″	84.8	6.8	0.7	98.8	0.5
0.03	″	75.3	6.8	0.7	98.8	0.5
0.09	20°	98.2	6.1	1.2	98.5	0.3

Table 3 Aluminium alkyl variation

Catalyst Addition Order	Ratio	Temperature (°C)	Level mM Nd/100g	Conv. %	Trans %	Cis %	Vinyl %	Comment
AlEt$_2$Cl + NdV$_3$ + MgBu$_2$	15 : 1 : 10	50°	0.09	97.1	1.6	98.0	0.4	Hazy, stable yellow solution
AlEt$_2$Cl + NdV$_3$ + MgBu$_2$	15 : 1 : 10	20°	0.09	98.2	1.2	98.5	0.3	″
AlEtCl$_2$ + NdV$_3$ + MgBu$_2$	7.5 : 1 : 10	50°	0.09	98.6	1.2	98.4	0.4	″
AlEtCl$_2$ + NdV$_3$ + MgBu$_2$	7.5 : 1 : 10	20°	0.09	98.6	0.6	99.0	0.4	″
Al$_2$Et$_3$Cl$_3$ + NdV$_3$ + MgBu$_2$	10 : 1 : 10	50°	0.09	97.9	1.2	98.1	0.7	″
Al$_2$Et$_3$Cl$_3$ + NdV$_3$ + MgBu$_2$	10 : 1 : 10	20°	0.09	96.2	0.9	98.6	0.5	″
NdV$_3$ + MgBu$_2$ + AlEt$_2$Cl	1 : 10 : 14	50°	0.26	89.8	8.0	91.4	0.6	Hazy, stable yellow
NdV$_3$ + MgBu$_2$ + AlEt$_2$Cl	1 : 10 : 19	50°	0.26	55.9	10.7	88.3	1.0	White ppt in 1-2 mins.
NdV$_3$ + MgBu$_2$ + AlEt$_2$Cl	1 : 10 : 22	50°	0.26	50.0	8.4	91.1	0.5	″
NdV$_3$ + MgBu$_2$ + AlEtCl$_2$	1 : 10 : 8.5	50°	0.26	69.8	4.7	94.7	0.6	″
NdV$_3$ + MgBu$_2$ + AlEtCl$_2$	1 : 10 : 7.5	50°	0.26	98.3	4.2	95.0	0.8	Hazy, yellow.
NdV$_3$ + MgBu$_2$ + AlEtCl$_2$	1 : 10 : 6.2	50°	0.26	98.8	5.0	94.2	0.8	″

(Polymerization time = 16 h)

obtained. In addition it was realized that didymium, with a constitution of approximately 72% Nd, 20% La and 8%, contained one component, lanthanum, which had been found[11] to be some 80% less active in *cis* polymerization than neodymium or praseodymium. Changing to neodymium versatate as rare earth compound gave a further increase both in catalytic activity and in *cis* content of the polymer. At maximum, it was now possible to get nearly 100% conversion to 98% *cis* polymer with 0.05mM Nd/100 g butadiene. Some typical experiments are summarized in *Tables 1* and *2*. The direct comparisons between didymium and neodymium were only run for

45 min in order to show up rate differences. Although aluminium ethyl sesquichloride had been used initially, other aluminium alkyl chlorides were equally effective at the correct ratio. Experiments were made with the original order of addition in which the ratios of AlEtCl$_2$ or AlEt$_2$Cl were varied against constant neodymium versatate and magnesium dibutyl concentrations (*Table 3*). There was little to choose between the alkyls under optimum conditions for each, with regard to conversion or *cis* content of the polymer. At too low a ratio of Al:Nd, *cis* content and conversion were reduced while at too high a ratio the catalyst partly or completely precipitated from

Table 4

Ratio of components Al : Nd : Mg	Ratio of Al : Mg	Conv. %	Intrinsic viscosity	Trans %	Cis %	Vinyl %	Comment
22.5 : 1 : 15.0	1.5 : 1	93.0	5.7	5.5	93.9	0.6	Lumps formed
18.7 : 1 : 12.5	1.5 : 1	93.4	5.6	4.4	94.9	0.7	initially later dispersed
15.0 : 1 : 10.0	1.5 : 1	97.8	7.8	1.3	98.4	0.3	Normal
11.3 : 1 : 7.5	1.5 : 1	91.9	5.9	1.9	97.6	0.5	Clearer, nearly
7.5 : 1 : 5.0	1.5 : 1	89.7	8.8	1.1	98.5	0.4	colourless
3.8 : 1 : 2.5	1.5 : 1	1.9	–	1.2	98.1	0.7	–
Al : Nd : Mg	Al : Nd	Conv.	Intrinsic viscosity	Trans	Cis	Vinyl	Comment
15 : 1 : 7.5	15 : 1	98.8	5.5	1.5	98.2	0.3	Normal
15 : 1 : 6.3	15 : 1	99.3	6.2	1.2	98.4	0.4	Normal
15 : 1 : 3.2	15 : 1	4.7	–	–	–	–	Partial ppt
15 : 1 : 2.5	15 : 1	0.7	–	–	–	–	Complete
15 : 1 : 1.3	15 : 1	Trace	–	–	–	–	precipitation

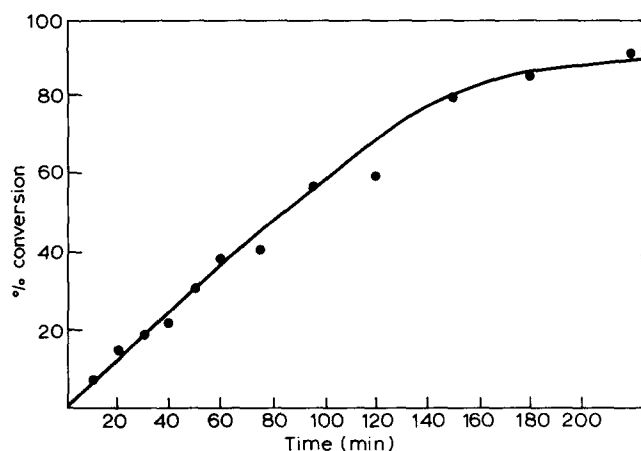$50°C$ for 16 h. [Nd] = 0.09 mM/100g Bd. Al Alkyl = $AlEt_2Cl$.

Figure 1 Nd=0.09 mM/100g Bd $AlEt_2Cl$: NdV_3 : $MgBu_2$= 15 : 1 : 10. Temperature=20°C

solution as a white flocculent solid although some catalytic activity was still retained. At the correct ratio the catalyst components added to the butadiene/hexane mixture formed a yellowish, cloudy, but stable system. Initially the cloudiness and white precipitate were attributed to formation of insoluble $MgCl_2$ but later experiments showed that under conditions where hexane solvent resulted in cloudiness, toluene as solvent produced perfectly clear solutions and it may be that the solid is a magnesium complex of the type $Mg[AlR_nX_{4-n}]_2$. The results in *Table 3* show that it is not the Al:Nd ratio which is critical but the Cl:Nd ratio with an optimum value between 12:1 to 17:1. The three aluminium alkyl halides have been compared directly using the best order of addition at a ratio of Cl:Nd of 15:1 (Cl:Mg=1.5:1). There is a marginal increase in *cis* content with decrease in polymerization temperature and an increase in *cis* also occurs with decrease in catalyst concentration (*Table 2*).

Apart from varying the aluminium alkyl and its concentration with respect to neodymium, it is also possible to change other ratios advantageously to give a reduction in total metal alkyl required, whilst still retaining high activity and *cis* content. Some results from experiments on this theme are recorded in *Table 4* where two components have been varied together against the third, or one has been varied against the other two (the

effect of changing $Al_2Et_3Cl_3$ ratio with respect to fixed Nd:Mg ratio was given in the upper half of *Table 1*).

It is apparent that altering the total alkyl with respect to neodymium either up or down is not beneficial and confirms the previous comment that the chloride to neodymium ratio is crucial. However, the amount of magnesium alkyl can be reduced substantially if the aluminium level is kept constant. Using aluminium diethyl chloride, the normal Al:Mg:Nd ratio of 15:10:1 can be changed to 15:6:1 without affecting conversion, *cis* content or molecular weight, thus reducing magnesium alkyl usage by nearly 50%. Below this level the catalyst rapidly becomes unstable confirming that the magnesium alkyl is a necessary component and that the aluminium to magnesium ratio is also important in the formation of stable catalyst mixtures.

A very surprising feature of the polymerizations was that the solutions became quite viscous within 2–3 min of adding the catalyst, even at low catalyst concentrations. The behaviour was quite unlike that shown by other rare earth catalyst systems, e.g. Nd butoxide – $AlEtCl_2$ – $AlBu_2H$[9]. At first this was attributed to extremely rapid rates of polymerization but there was no corresponding large exotherm. When rate experiments were carried out, the overall time to 100% conversion was found to be similar to that obtained with other high *cis* catalysts. Unlike the latter, however, which showed S-shaped curves for conversion *versus* time, the magnesium based systems showed little, if any, slow induction period (*Figure 1*). The data are scattered as a result of working with high viscosity unstirred solutions but, like the *trans* polymerizations, the *cis* polymerizations showed first order dependency on monomer (*Figure 2*) in the later stages of polymerization. However, in the early stages, the plot followed a different curve.

Like the *trans* and other rare earth high *cis* catalysts, molecular weight of the polymer increased linearly (*Figure 3*) with conversion to over 70% indicating the presence of live chain ends. However, the broad distribution (>5) and the fact that the line does not extrapolate to zero indicate that this is not strictly a living polymer system. Peak molecular weight at 60% conversion was over one million indicating a low level of chain termination but interestingly molecular weights of
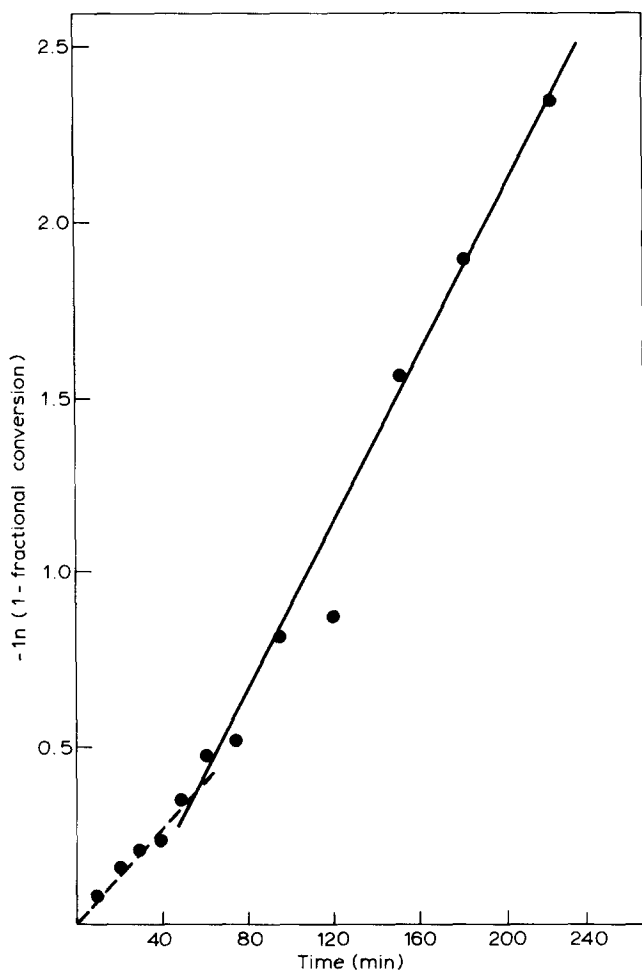
Figure 2 Nd = 0.09 mM/100g Bd AlEt$_2$Cl : NdV$_3$:MgBu$_2$ = 15 : 1 : 10. Temperature = 20°C

300 000 were recorded within 5 min of adding the last catalyst component.

The work on *cis* polymerization catalysts was started by chance when a Lewis acid, Al$_2$Et$_3$Cl$_3$, was added in an attempt to modify the microstructure of polymer obtained with the basic MgBu$_2$-rare earth catalyst. Experiments were carried out with other Lewis acids to see if they had the same effect and whether the extra alkyl groups were necessary. PCl$_3$ and POCl$_3$ caused formation of white precipitates and did not yield active catalysts either as replacements for aluminium alkyl halide or in combination with aluminium trialkyl. SiCl$_4$, MeSiCl$_3$ and TiCl$_4$ all proved capable of polymerizing butadiene, in the presence of MgBu$_2$ and didymium versatate, to low conversion and reasonably high *cis* content although TiCl$_4$ was reduced *in situ* to TiCl$_3$ and formed a high proportion of gel. CCl$_4$, as a halogenated Group IV compound with no acidic properties and no alkyl group gave similar results. All these catalysts gave considerable improvement in conversion when AlBu$_3$ was added as a fourth catalyst component (*Table 5*). In all cases it was necessary to use at least 0.26 mM Nd/100 g Bd.

Although it is likely that both CCl$_4$/AlBu$_3$ and SiCl$_4$/AlBu$_3$ combinations would have given better results if they had been more fully investigated, the initial results with MeSiCl$_3$ suggested that this was the most promising candidate for further experiments. The results in *Table 6* show that high conversion of butadiene was

possible, to give polymer with a reasonable *cis* content although higher *cis* could be obtained at lower conversion using lower catalyst levels. The experiments with AlBu$_2$H were tried because the hydride group might have produced lower molecular weight polymer via the Al–H bond or through exchange of groups with MeSiCl$_3$. Changing the order of addition of catalyst components had virtually no effect on polymerization, i.e. the polymerization still required a high level of catalyst for good conversion.

Unlike the *trans* catalyst system, the *cis* catalyst produced polybutadiene with a high molecular weight and broad distribution, which although suitable for compounding into an oil extended rubber did not give satisfactory processing as a straight tyre rubber. The material as produced in bottles by laboratory techniques was a tough rubbery lump to which it was difficult to add antioxidant or to kill off easily with methanol. Three mechanisms were possible for the high molecular weights obtained. (1) Lack of chain transfer which might be overcome by adding one of the known transfer agents. (2) Very slow initiation, resulting in a broad range of molecular weights. In this connection 'seeding' techniques were considered, i.e. formation of a low molecular weight polybutadiene using a normal concentration of catalyst and a small weight ($\simeq 0.5$ g) of butadiene monomer, with addition of the remaining butadiene after completion of the initial reaction. Using the catalyst neodymium versatate – AlEtCl$_2$ – AlBu$_3$, which suffered from the same molecular weight problem, seeding did not help and indeed the seed polymer itself had a remarkably wide distribution with molecular weight ranging from about 10 000 to over one million and $M_w/M_n = 22$! (3) A variety of different types of catalyst centre might be present, capable of different rates of polymerization. This kind of situation has been considered responsible[13] for the narrow distribution of syndiotactic polypropylene at $-78°C$ compared to formation of broad molecular weight isotactic polymer produced at greater than $-20°C$ with the catalyst VCl$_4$–AlEt$_2$Cl. With the present catalyst it might help to use rare earth compounds with only one possible active site on an atom instead of three, e.g. (cp)$_2$NdCl or (cp)$_2$Nd versatate instead of Nd(versatate)$_3$. It could also be, since the initiating system in hexane is cloudy, that some of the molecular weight broadening is due to the formation of a partly heterogeneous catalyst. Certainly at
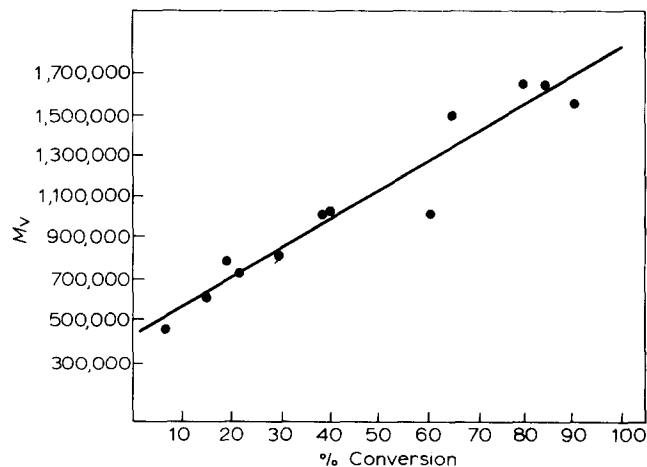

Figure 3 Nd = 0.09 mM/100g Bd AlEt$_2$Cl : NdV$_3$: MgBu$_2$ = 15 : 1 : 10. Temperature = 20°C

Table 5

Halide	Didym. vers. : Mg : AlBu$_3$: halide	% conversion	IV	Trans %	Cis %	Vinyl %
MeSiCl$_3$	0.1 : 1 : 1.2 : 0.75	77.5	2.81	5.8	93.4	0.8
	0.1 : 1 : 1.2 : 0.9	77.2	2.84	5.8	93.5	0.7
	0.1 : 1 : 1.2 : 1.05	80.9	2.37	5.6	93.7	0.7
	0.1 : 1 : 1.2 : 1.2	77.2	3.20	7.4	91.9	0.7
	0.1 : 1.75 : 0 : 1.75	19.0	—	4.2	95.3	0.5
	0.1 : 1.75 : 0 : 0.75	15.1	—	92.6	5.9	1.5
	0.1 : 0 : 2.0 : 1	49.4	—	13.4	86.2	0.4
	0.05 : 0 : 2.0 : 0.04	11.9	—	10.2	87.9	1.9
SiCl$_4$	0.1 : 1 : 0 : 1	0.6	—	5.5	85.6	8.7
	0.1 : 1 : 0 : 0.5	5.3	—	6.0	92.5	1.5
	0.1 : 1 : 1.2 : 1	53.3	1.92	9.8	89.6	0.6
	0.1 : 1 : 1.2 : 1.5	40.2	5.67	3.4	96.0	0.6
	0.1 : 1 : 1.2 : 2	38.9	5.78	1.6	97.7	0.7
CCl$_4$	0.1 : 1 : 0 : 1	4.5	—	9.6	88.5	1.7
	0.1 : 1 : 0 : 0.5	3.4	—	38.5	58.8	2.7
	0.1 : 1 : 0 : 0.25	22.3	—	94.3	3.6	2.0
	0.1 : 1 : 1.2 : 1	28.1	—	14.5	84.1	1.4
				(Soluble portion)		
TiCl$_4$	0.1 : 1 : 0 : 1	47.7	—	27.1	71.4	1.5
	0.1 : 1 : 0 : 0.5	38.0	—	35.5	52.2	12.3
	0.1 : 1 : 0 : 0.25	9.3	—	15.0	30.7	54.1
	0.1 : 1 : 1 : 1	87.2	—	53.0	32.0	14.8

50°C for 16 h. [Nd] = 0.26 mM/100g Bd.

Table 6 Use of MeSiCl$_3$

Catalyst	Ratio	Level mM Nd per 100g Bd	Conv. %	Intrinsic viscosity	Trans %	Cis %	Vinyl %
AlBu$_3$ + MeSiCl$_3$ + NdV$_3$ + MgBu$_2$	12.5 : 7 : 1 : 10	0.26	71.6	1.75	27.5	71.6	0.9
" " " "	12.5 : 9 : 1 : 10	0.26	86.4	2.36	13.4	86.4	0.2
" " " "	12.5 : 11 : 1 : 10	0.26	87.5	2.47	12.2	87.5	0.3
" " " "	12.5 : 13 : 1 : 10	0.26	90.1	2.81	9.6	90.1	0.3
" " " "	12.5 : 15 : 1 : 10	0.26	89.4	2.52	10.2	89.4	0.4
" " " "	12.5 : 17 : 1 : 10	0.26	90.6	2.65	9.0	90.6	0.4
" " " "	12.5 : 20 : 1 : 10	0.26	96.5	3.41	6.7	92.8	0.5
" " " "	12.5 : 22 : 1 : 10	0.26	97.5	2.84	7.4	92.1	0.5
NdV$_3$ + MgBu$_2$ + AlBu$_3$ + MeSiCl$_3$	1 : 10 : 12.5 : 13	0.26	83.6	3.89	5.8	93.9	0.3
" " " "	1 : 10 : 12.5 : 17	0.26	87.3	3.44	5.3	94.2	0.5
AlBu$_2$H + MeSiCl$_3$ + NdV$_3$ + MgBu$_2$	12.5 : 13 : 1 : 10	0.26	98.0	3.18	4.9	94.9	0.2
" " " "	12.5 : 13 : 1 : 10	0.26	98.2	2.95	4.7	95.0	0.3
AlBu$_3$ + MeSiCl$_3$ + NdV$_3$ + MgBu$_2$	12.5 : 20 : 1 : 10	0.18	78.9	—	6.0	93.6	0.4
" " " "	12.5 : 20 : 1 : 10	0.09	38.7	—	4.0	95.7	0.3
AlBu$_2$H + MeSi Cl$_3$ + NdV$_3$ + MgBu$_2$	12.5 : 15 : 1 : 10	0.18	72.0	—	2.7	97.0	0.3
" " " "	12.5 : 15 : 1 : 10	0.09	35.1	—	2.1	97.5	0.4
NdV$_3$ + MgBu$_2$ + AlBu$_3$ + MeSiCl$_3$	1 : 10 : 12.5 : 15	0.18	80.9	—	2.0	97.6	0.4
" " " "	1 : 10 : 12.5 : 15	0.09	42.7	—	1.9	97.8	0.3

Temperature = 50°C. 0.26 mM levels run for 16 h, lower levels for 48 h.

high ratios of aluminium alkyl halide to neodymium where catalyst precipitation occurred, some polymer was associated with the precipitate and some with the clear solution.

The attempts to alter molecular weights and distribution reported here were concerned with the addition of various potential chain transfer agents. While the work was in progress, similar work was reported[14] in which ethanol, dihydronaphthalene, chloroform, diethyaniline, triphenylmethane, octanoic acid, allyl iodide and diallyl ether were unsuccessfully tried. Molecular weight increased or decreased but in all cases the conversions were reduced. This behaviour is generally similar to that experienced with high *cis* polybutadiene catalysts based on nickel[15,16] although in those cases the unmodified molecular weights were much lower than with rare earth catalysts. The results with additives detailed in *Table 7* show a similar trend. Hydrocarbon additives had very little effect while the more reactive compounds reduced conversion. Of the additives tried, 1,2 butadiene is a known controller of gel in lithium butyl polymerization[17] and has been patented[18] as a modifier for Ziegler catalysis. Zinc diethyl has been used as a replacement for hydrogen to modify polyethylene and EP copolymer

Table 7

Modifier	Propylene level on Bd	% conversion	Intrinsic viscosity	Trans %	Cis %	Vinyl %
Propylene added	0	97.3	5.97	1.9	97.6	0.5
before catalyst	500 ppm	95.9	6.98	1.9	97.3	0.8
	1000 ppm	95.3	7.28	2.6	96.7	0.7
	1500 ppm	94.5	7.03	2.0	97.5	0.5
	2000 ppm	92.0	7.39	3.2	95.5	1.3

Modifier	1, 2 Bd on 1, 3 Bd	% conversion	Intrinsic viscosity	Trans %	Cis %	Vinyl %
1,2 Butadiene	0	95.9	6.46	2.3	97.3	0.5
added before	500 ppm	95.6	6.36	3.1	96.3	0.6
catalyst	1000 ppm	96.2	6.34	2.6	96.7	0.7
	2000 ppm	96.1	6.56	2.3	97.1	0.6

Modifier	Mole ratio Zn to Nd	% conversion	Intrinsic viscosity	Trans %	Cis %	Vinyl %
ZnEt$_2$ added after	0 : 1	98.7	5.63	—	—	—
aluminium but	1 : 1	99.4	5.04	1.2	98.5	0.3
before Nd	3 : 1	98.8	6.51	1.4	98.2	0.4
	5 : 1	98.2	5.73	1.3	98.0	0.7
	10 : 1	98.2	5.82	2.0	97.4	0.6
	15 : 1	98.1	6.72	1.4	98.0	0.6

Modifier	O$_2$ on Bd	% conversion	Intrinsic viscosity	Trans %	Cis %	Vinyl %
Oxygen added	0 ppm	98.6	—	—	—	—
before catalyst	500 ppm	6.1	—	—	—	—
	750 ppm	0	—	—	—	—
	1000 ppm	0	—	—	—	—
	1500 ppm	0	—	—	—	—

Modifier	Hexadiene on Bd	% conversion	Intrinsic viscosity	Trans %	Cis %	Vinyl %
1,5 Hexadiene	600 ppm	98.7	6.71	2.1	97.4	0.5
added before	1200 ppm	99.3	6.87	2.6	96.7	0.7
catalyst	2400 ppm	98.7	6.43	2.2	97.1	0.7
	4800 ppm	98.2	0.71	2.7	96.7	0.6
	9600 ppm	98.0	6.96	2.3	97.1	0.6
	12000 ppm	98.1	6.64	2.3	97.3	0.4

Modifier	Mole ratio ETCA to Nd	% conversion	Intrinsic viscosity	Trans %	Cis %	Vinyl %
Ethyl trichloracetate	0 : 1	100	6.17	—	—	—
added after Al and	1 : 1	98.8	6.25	1.0	98.5	0.5
before Nd.	3 : 1	39.5	8.27	1.3	98.1	0.6
	5 : 1	3.4	7.10	1.2	98 3	0.5

Modifier	Mole ratio BuOH to Nd	% conversion	Intrinsic viscosity	Trans %	Cis %	Vinyl %
n-Butanol modifier	0 : 1	98.7	5.80	—	—	—
added after all	1 : 1	100.0	5.67	1.3	98.1	0.6
catalyst components	2.5 : 1	97.7	6.14	1.3	98.0	0.7
	5 : 1	97.5	5.26	1.1	98.4	0.5
	7.5 : 1	95.4	4.00	1.1	98.3	0.6
	10 : 1	48.3	7.51	1.0	98.5	0.5
n-Butanol modifier	1 : 1	99.3	5.80	2.0	97.5	0.5
added after Nd and	2.5 : 1	99.4	4.68	1.9	97.7	0.4
before Mg	5 : 1	98.7	5.22	1.0	98.5	0.5
	7.5 : 1	99.3	5.82	1.0	98.6	0.4
	10 : 1	94.7	7.62	0.9	98.5	0.6

Time : 16 h   [Nd] = 0.09 mM/100g Bd.   Temp. = 50°C.

molecular weights and ethyl trichloroacetate has been used for the same purpose[19,20]. α-ω dienes have recently been claimed[21] as modifiers for nickel catalysed high *cis* polybutadiene with 1,5-hexadiene as the most effective compound exemplified. Finally oxygen and alcohols have been tried in, and claimed as, successful modifiers for various types of hydrocarbon polymerization.

With regard to the more active additives, zinc dialkyl has no effect at all and since it is so similar to magnesium alkyl it probably acts simply as an extra source of alkyl

Table 8 Modification with toluene

Catalyst (0.09 mM Nd/100g Bd)	% w/w toluene on hexane	% conversion	Intrinsic viscosity toluene at 30°C	Trans %	Cis %	Vinyl %
AlEt₂Cl + NdV₃						
+ MgBu₂	0	97.9	6.22	2.1	97.2	0.7
15 : 1 : 10	2.5	98.8	6.61	2.7	96.9	0.4
16 h at 50°C	5.0	97.4	6.04	2.6	96.9	0.5
	10.0	97.4	6.53	2.0	97.7	0.3
	20.0	98.6	5.44	2.1	97.5	0.4
	100.0	98.1	3.58	2.2	97.3	0.5

[Nd] = 0.09 mM/100g Bd.   Temp. = 50°C.

groups in the system. In ethylene or ethylene–propylene polymerization ETCA and similar chlorinated esters are thought to react by reoxidizing reduced vanadium species by adding a chloride ligand to divalent vanadium before realkylation. In rare earth systems there is little chance of metal compound reduction and the results suggest that ETCA is destroying active centres. Oxygen reacts to form alkoxides from the metal alkyls of Mg and Al and thus has probably destroyed the catalyst at the relatively low levels used. Butanol also reacts with metal alkyls to form alkoxides but the highest level used in the experiments was sufficient to react with approximately only one metal alkyl bond and therefore catalytic activity was retained. The two orders of addition were designed to allow the butanol to react (a) with the aluminium before addition of the magnesium or (b) with either or both of the aluminium and magnesium alkyls. Although the lack of effect at these levels is surprising, rare earth catalysts are known in which the rare earth compound is activated by an alcohol[22].

A J.S.R. patent[23] describes the use of toluene as an effective modifier for a typical rare earth high *cis* catalyst with a claim for reduction of Mooney viscosity from 134 with no toluene present, to 21 in 100% toluene. Experiments with the magnesium based catalyst (*Table 8*) show that toluene only has a marked effect when used as total solvent for the polymerization but even then the resulting molecular weight was still high (M_v from intrinsic viscosity $\simeq 580\,000$). Hydrocarbons with a more acidic hydrogen might have been more effective but Ph_3CH[13] was shown to increase molecular weight and decrease conversion in a similar system, although the J.S.R. Patent[23] claims that xylene, dihydronaphthalene and mesitylene are effective in lowering Mooney viscosity whilst retaining 100% conversion. With the present catalyst 1,2 dihydronaphthalene decreased conversion and increased molecular weight but the effect was only noticeable at high concentrations of additive. As noted previously, when the catalyst components were mixed with toluene in the presence of butadiene a clear yellow solution was obtained, in contrast to the cloudy product in hexane.

THF had no effect on the microstructure of polybutadiene prepared with the *trans* catalyst (c.f. Part 1). THF also had little effect on the catalyst Nd versatate–AlEtCl₂–AlBu₂H at ratios up to THF:Nd of 10:1 although an increase in molecular weight and some gel formation accompanied by a reduction in conversion was

noted at the highest ratio used. The *cis* content remained between 98 and 99%. It was surprising in view of the latter result that the magnesium based high *cis* catalyst was converted to a catalyst producing a moderate yield of high *trans* butadiene when THF was added at a THF-Nd ratio of 10:1. The effect was only noticeable when using the 'standard' Nd:Mg ratio of 0.1:1 and Cl:Nd of 15:1. With more aluminium alkyl halide the catalyst produced high *cis* polymer. It appears that the Lewis base, THF, and the Lewis acid react together at a molar ratio of 1:1 leaving the two other catalyst components MgBu₂ and Nd versatate unaffected in their ability to produce *trans* polymer.

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