Butadiene polymerization with a rare earth compound using a magnesium alkyl cocatalyst: 1.

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High *trans* polybutadiene was obtained using a catalyst system comprising rare earth compounds plus magnesium dialkyl. The polymer appeared to contain some 'live' chain ends and block polymerization and coupling experiments were carried out. High *cis* polybutadienes formed when aluminium alkyl halides were used as a third catalyst component.

INTRODUCTION

With the recent upsurge of interest in rare earth compounds as commercially viable diene catalysts[1-4] it was of interest to determine the microstructures of polybutadienes made with a mixture of rare earth compound and alkyls other than aluminium. Most of the catalysts based on rare earths and aluminium alkyls or alkyl halides had produced polybutadiene with an exceptionally high *cis* content. One catalyst yielding high *trans* polybutadiene had been described[5]; this was made using a rare earth allyl compound stabilized as the lithium salt Li (RE allyl)$_4$, with Al halides or alkyl halides. However, a recent European patent[6] describes the preparation of a rare earth compound from neodymium metal and allyl choride, in which some kind of allyl neodymium is presumably formed *in situ*, and this gives high *cis* polybutadiene when used with aluminium alkyl hydride.

EXPERIMENTAL

Butadiene (99.8%) was distilled through a KOH pellet column to remove inhibitor and then through three alumina drying columns into 250 ml glass bottles containing 75 mls dry solvent under nitrogen to make approximately 20% wt/volume solutions. The bottles were sealed with heptane extracted butyl rubber liners and crown caps. Styrene was distilled under vacuum at 30°C, once through a column containing KOH pellets topped with 3 Å molecular sieves and then again through a 3 Å sieve column. It was added to bottles in the required quantities by syringe.

Aluminium alkyls (Schering A.G.) and magnesium n-butyl, isobutyl (Lithco) were used as received and diluted with dry hexane. All catalyst components were added by syringe.

Hexane (BDH, SLR grade) was redistilled under dry nitrogen from a small quantity of butyl lithium, and transferred by nitrogen pressure to capped, dried bottles.

Rare earth versatates were prepared by treating a rapidly stirred aqueous solution of the rare earth halide with three equivalents of sodium versatate added drop-wise (Shell 'Versatic 10' with one equivalent of NaOH in H$_2$O). The resulting whitish sticky precipitate was extracted with toluene, dried *in vacuo* and redissolved in pure dry hexane.

Molecular weights and distributions were run on a Dupont 870 Gel Permeation Chromatograph using THF solvent. The high *cis* polymers tended to block the g.p.c. columns even after filtration through an 0.2 μm filter or treatment with calcium sulphate. Infra-red spectra were obtained from films cast onto KBr discs from chloroform solution.

Polymerizations were carried out in unstirred bottles in a thermostatically controlled water bath. The resulting polymers were poured into, or mixed with, (*trans* polymer insoluble in hexane at 25°C) methanol containing antioxidant and dried *in vacuo*.

RESULTS AND DISCUSSION

Initial experiments were carried out with 'didymium' versatate (didymium refers to a rare earth mixture containing approximately 72% Nd, 20% La and 8% Pr) and a mixture of magnesium dialkyl and aluminium triethyl in a molar ratio of 1:0.19 this being the ratio in a commercial soluble 'magnesium' alkyl. It was soon found that the aluminium trialkyl had no effect on microstructure or conversion of polybutadiene and in subsequent experiments magnesium dialkyl was used alone as cocatalyst. For *trans* polymerization of butadiene, didymium versatate and neodymium versatate gave very similar results (although this was not the case for *cis* polymerization—cf Part 2). Some typical results are given in *Table 1*. Conversions generally only reached 65-75% at 50°C in 16 h and this level of conversion was maintained even when the catalyst level was increased by 50%. Conversions were reduced at lower catalyst levels. The catalyst ratio appeared to be very critical and reduced conversions were obtained both above and below the optimum of Mg:rare earth = 1:0.1. Molecular weights were low, with peak values of about 50 000-80 000 and the distributions were surprisingly narrow with $M_w/M_n = 1.5$.

Table 1

Solvent	Rare earth: versatate	AlEt$_3$: (molar ratio)	MgBu$_2$	Conv. %	Trans %	Cis %	Vinyl %
Hexane		0.2 :	0.19 :	1	12.9	78.3	18.0	3.7
"		0.1 :	0.19 :	1	63.3	90.3	6.4	3.3
"	'Didymium'	0.05 :	0.19 :	1	61.9	95.2	2.6	2.2
"		0.1 :	1 :	0	2.0	54.4	39.6	5.9
"		0.12 :	0 :	1	13.3	92.3	5.4	2.3
"		0.1 :	0 :	1	81.3	96.9	0.9	2.2
"		0.06 :	0 :	1	77.9	97.8	0.8	1.4
"	Nd	0.1 :	0 :	1	59.9	96.4	0.8	2.8
"		0.1 :	0 :	1.5	9.7	89.2	7.2	3.6
		0.075 :	0 :	1	23.7	95.1	2.6	2.3
Toluene	Nd	0.1 :	0 :	1	64.1	96.3	1.8	1.9

Polymerization for 16 h at 50°C.
Nd = 0.26 mM/100g butadiene.

Table 2

	Versatate: (molar ratio)	AlEt$_3$:	MgBu:	THF	Conv. %	Trans %	Cis %	Vinyl %
	0.1 :	0.19 :	1 :	0	67.9	96.2	1.7	2.1
	0.1 :	0.19 :	1 :	0.2	83.1	97.6	0.7	1.7
	0.1 :	0.19 :	1 :	0.6	83.4	98.7	0.3	1.0
'Didymium'	0.1 :	0.19 :	1 :	1.2	83.6	98 2	0.3	1.5
versatate	0.1 :	0.19 :	1 :	2.4	75.0	96.8	1.2	2.0
	0.1 :	0.19 :	1 :	4.8	57.4	96.9	1.4	1.7
	0.1 :	0.19 :	1 :	7.2	35.3	94.3	3.0	2.7
	0.1 :	0.19 :	1 :	9.6	25.3	94.8	3.3	1.9
	0.1 :	0 :	1 :	0	66.4	93.8	2.9	3.3
Neodymium	*0.1 :	0 :	1 :	0	74.8	---	—	—
versatate	0.1 :	0 :	1 :	0.5	85.1	91.7	4.5	3.8
	0.1 :	0 :	1 :	0.75	88.5	90.3	4.5	5.2
	0.1 :	0 :	1 :	1.0	89.3	95.3	2.5	2.2
	0.1 :	0 :	1 :	1.5	90.9	83.5	14.8	0.7

Polymerization for 16 h at 50°C [Nd] = 0.26 mM/100 g Bd.
* [Nd] = 0.39 mM/100 g Bd.

With Ziegler type catalysts it is often possible to increase molecular weight by operating at low temperatures but this was not possible in the present instance because of polymer insolubility.

One object of the work was to find a catalyst capable of producing polybutadiene and styrene butadiene random copolymers with about 70% *trans* content and various additives were tried in the rare earth/MgBu$_2$ system in order to alter the *trans* content of the polymer.

THF was chosen as a typical Lewis base, well documented for its ability to increase the vinyl content of polybutadiene in alkyl lithium initiated anionic polymerization. Among the rare earth catalyst systems reported for the preparation of high *cis* polybutadiene, some[7] have used THF as a component with no apparent effect on microstructure. In the rare earth versatate/MgBu$_2$ system small amounts of THF enhanced the *trans* content slightly. At higher levels, *trans* decreased, *cis* increased but vinyl content remained unchanged. Conversion increased significantly at low THF levels but decreased rapidly above a ratio of MgBu$_2$:THF of 2.5:1 as shown in *Table 2* for the didymium catalyst. The effect on the neodymium catalyst with no added aluminium alkyl was similar but lower *trans* contents were recorded. Other polar compounds were tested and (ō-dimethoxy benzene) gave a similar enhanced conversion at a ratio of Nd:modifier:Mg of 0.1:0.5:1, but hexamethylphosphoramide killed the polymerization and dipiperidinoethane decreased conversion, at the same ratio.

Since Lewis bases had little effect on microstructure, a Lewis acid, Al$_2$Et$_3$Cl$_3$, was tried. At a ratio of Nd:Al:Mg of 0.1:1.5:1 good yields of high *cis* polymer were obtained and a full description of this and other high *cis* catalysts will be given in Part 2 of this series of papers.

Another way in which the high *trans* microstructure might be altered would be by the addition of lithium butyl which gives about 50% *trans*, 40% *cis* and 10% vinyl for polybutadienes prepared in hydrocarbon solvents. The problem is whether one homopolymer or a mixture of two would result. As shown in *Table 3*, addition of sufficient lithium butyl both enhances the conversion and alters the microstructure until it becomes similar to that obtained with lithium alkyl alone. In the absence of magnesium alkyl, the catalyst produces very low conversions of polymer with the microstructure expected for lithium butyl alone. G.p.c. traces showed a peak with narrow distribution and no obvious bimodality.

Few catalysts producing very high *cis* or *trans* polybutadiene microstructures are capable of copolymerizing butadiene and styrene. For those that do[8,9], it has been reported that incorporation of styrene decreases the *cis* content in polymers produced with nickel based catalysts

Table 3

Didym(vers)$_3$:	LiBu: (molar ratio)	MgBu$_2$	Conv. %	I.V.	Trans %	Cis %	Vinyl %
0.6	: 0.05	: 1	91.7	0.95	94.7	2.0	3.3
0.06	: 0.1	: 1	93.4	0.91	97.2	0.7	2.1
0.06	: 0.2	: 1	94.9	0.83	97.7	0.4	1.9
0.06	: 0.5	: 1	94.3	0.70	95.1	2.6	2.3
0.06	: 0.6	: 1	93.4	—	71.5	22.7	5.8
0.06	: 0.8	: 1	96.2	—	58.9	33.7	7.4
0.06	: 1.0	: 1	99.0	—	55.0	36.1	8.9
0.06	: 1.2	: 1	96.9	—	53.4	37.5	9.1
*0.06	: 0.4	: 1	60.0	—	94.3	2.9	2.8
*0.06	: 0.6	: 1	63.0	—	89.4	7.2	3.4
*0.06	: 0.8	: 1	82.6	—	79.2	15.8	5.0
*0.06	: 1.0	: 1	88.6	—	68.4	25.3	6.3

Polymerization for 16 h at 50°C.
[Did] = 0.26 mM/100 g Bd.   * [Nd] = 0.19 mM/100g Bd
Intrinsic viscosities in toluene at 30°C.

Table 4

Didym(vers)$_3$:	MgBu$_2$:	LiBu	Conv. %	Trans %	Cis %	Vinyl %	St incorp. %
0.06	: 1	: 0	71.3	96.0	2.2	1.6	2
0.06	: 1	: 0.6	73.6	89.3	7.8	2.9	5.1
0.06	: 1	: 0.8	76.5	82.1	13.3	4.6	9.4
0.06	: 1	: 1.0	92.6	68.8	24.8	6.2	17.8
0.06	: 1	: 1.2	98.4	56.7	35.7	7.6	23.3
LiBu at 0.08 phm			98.1	49.2	42.1	8.7	24.2

Polymerization for 16 h at 50°C.
[Did] = 0.26 mM/100g Bd.
Styrene added = 25% by weight on butadiene.

Didymium (versatate)$_3$ + MgBu$_2$ at 50°C, 0.1:1
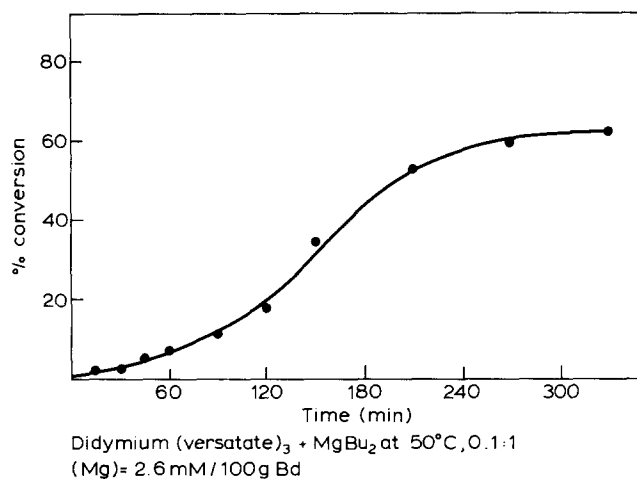(Mg)= 2.6 mM / 100 g Bd

Figure 1   Reaction rate

but that *cis* increases with styrene in cobalt catalysts. In the present work it has been found that although the high *trans* catalyst does not allow significant copolymerization of butadiene and styrene, increasing levels of lithium butyl cause increasing incorporation of styrene with block/random contents typical of an unmodified SBR polymerization with lithium butyl (see *Table 4*). Again it was not possible to distinguish *trans* homopolymer from normal lithium butyl SBR copolymer by g.p.c. although intuitively a mixture might be expected, instead of a single copolymer of decreasing *trans* content.

It was possible that at relatively low (70–80%) conversions using a non-randomized system, an unrealistic

figure for styrene incorporation was found. (In an unrandomized SBR polymerization with lithium butyl the majority of styrene is incorporated as a block at >85% total conversion.) Accordingly some polymerizations were carried out with rare earth versatate/MgBu$_2$/THF at a ratio of 0.1:1:1.2 assuming the THF to act as randomizing agent as in lithium butyl polymerizations. In all cases the amount of styrene incorporated was less than 2.5%. However, if THF does not affect the vinyl content of the polymer, as previously found, it seems likely that it is also not acting as a randomizing agent.

Work on rare earth catalysts for high *cis* polybutadiene and polyisoprene has demonstrated that the polymers contain a high proportion of 'live' chain ends[2] although other factors such as molecular weight distribution show that these are not 'living' polymers in the strictest sense. A rate run (*Figures 1, 2* and *3*) with the *trans* catalyst showed that molecular weight increased linearly with conversion up to about 50%, suggesting that this system too contains a high proportion of live chain ends. In addition, the active polymerizing solutions were bright yellow and the colours were discharged by the addition of methanol, which suggests either live chains (c.f. red colour of 'live' polystyrene/yellow colour of 'live' polybutadiene) or perhaps formation of unstable rare earth-alkyl bonds. In this context it seemed worth trying block polymerization to form an AB copolymer with styrene and coupling reactions with various halides to increase the molecular weight of *trans* polybutadiene.

Block styrene polymerizations were carried out under two sets of conditions. In the first method styrene was added to a fully polymerized butadiene 'cement' but since

previous experiments had shown that conversion was only around 70% at the completion of polymerization, a second method was used in which styrene was added at lower conversions after removing excess butadiene monomer. In all cases less than 1% styrene was found in the polymer, no characteristic polystyrene anion colour appeared and the original yellow colour of the polybutadiene remained.

Attempts were made to couple *trans* polymers using $SiCl_4$, $MeSiCl_3$, $CHCl_3$ and CCl_4 after polymerization had been completed. In some cases a slight decrease in the yellow colour of the cement was observed and some gel was produced with $SiCl_4$ but the isolated soluble material was of very similar molecular weight to the untreated polymer (from intrinsic viscosity and g.p.c. evidence).

The above two groups of experiments do not rule out the possibility of using live chain ends for further reaction. In particular, the addition of aluminium alkyl halides to the original two component *trans* catalyst to form a three component *cis* catalyst provided a unique opportunity to attempt the preparation of *trans–cis* block copolymers. Theyssie and coworkers[10], using allyl nickel trifluoracetate catalysts, obtained stereoblock polymers containing

cis and *trans* blocks, which had some thermoplastic elastomer properties. Japanese workers[11] have reported the preparation of a *cis–trans* AB block copolymer and a *cis*-1,2 block copolymer using different catalysts to obtain the two different blocks. Experiments were carried out in toluene with didymium versatate and magnesium alkyl as initial catalyst and aluminium ethyl sesquichloride added at predetermined times. Bottles were cooled to 25°C from 50°C before the addition and shaken for 1–2 min to disperse the alkyl before reheating to 50°C. Some gel formed, probably as a result of poor mixing, and the bright yellow colour of the *trans* catalyst faded to the pale cloudy yellow typical of the high *cis* catalyst. Later experiments were done in hexane to avoid any possibility of chain transfer to solvent. Polymerization results are given in *Table 5*. A g.p.c. of a typical product (*Figure 4*) showed a narrow peak with peak MW at about 60–70 000 with a lower broad high MW shoulder on the side. This would be expected for a mixture of *trans* and *cis* homopolymers. The broad shoulder increased in height with increased proportion of *cis* units in the product.

In contrast to the g.p.c. results, crude fractionation of the sample containing 51.4% *trans* units indicated probable block polymerization. 1 g polymer was sequentially extracted with the results shown in *Table 6*.

Nothing approaching a pure *cis* or *trans* polymer was isolated even although high *trans* polymer would be insoluble in the first five fractionation mixtures. The
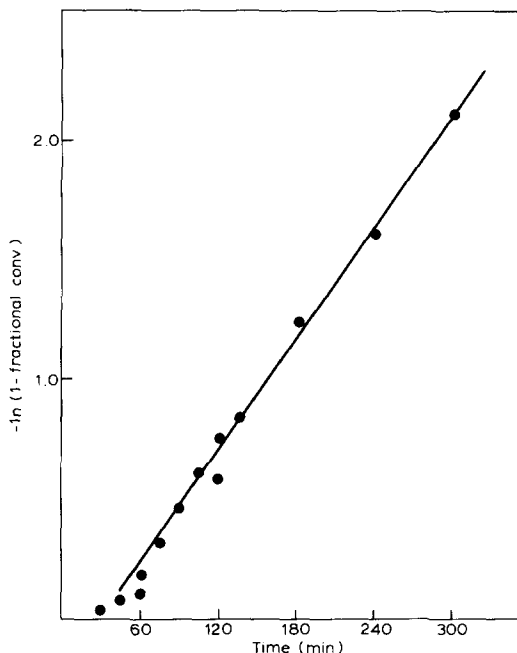

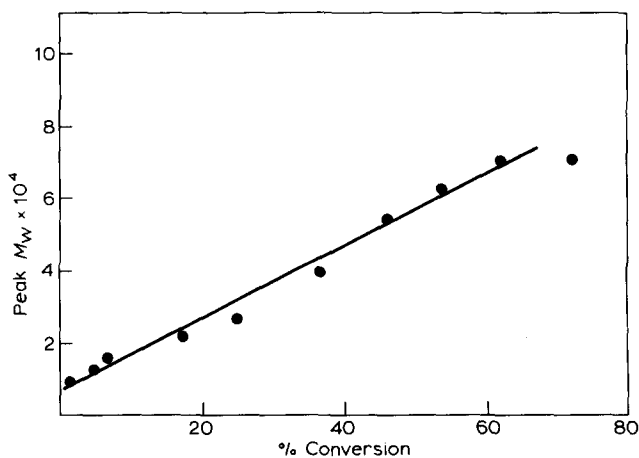**Figure 2** 1st order plot (with respect to monomer)

Figure 3 Peak M_w versus % conversion

Table 5

Solvent	Time of $Al_2Et_3Cl_3$ addition (min)	Conv. %	*Trans* %	*Cis* %	Vinyl %
Toluene	None added, polymerization stopped				
	at 90 min	48.9	96.2	1.7	2.1
	60 min	77.2	73.0	25.3	1.7
	90 min	73.1	78.4	20.0	1.6
	150 min	68.3	92.0	5.9	1.9
Hexane	30 min	78.1	18.6	80.5	0.7
	45 min	77.6	31.1	68.1	0.8
	60 min	89.1	51.4	47.6	1.0

[Did] = 0.25 mM/100g Bd.
Temp. = 50°C
Ratio Didym: Al : Mg = 0.1 : 1.5 : 1

Table 6

Solvent	Wt extract	Trans %	Cis %	Vinyl %
(1) MEK/hexane = 5 : 1 v/v	None	–	–	–
(2) MEK/hexane = 2 : 1	0.1 g	38.0	60.9	1.1
(3) MEK/hexane = 1 : 1	0.2 g	42.5	56.8	0.7
(4) MEK/hexane = 1 : 2	0.2 g	36.8	62.5	0.7
(5) Cold hexane (20°C)	0.06 g	67.7	31.2	1.1
(6) Hexane (Soxhlet)	0.24 g	75.2	23.9	0.9
(7) Toluene (Soxhlet)	0.1 g	48.7	50.0	1.3
(8) Chloroform	0	–	–	–
(9) Gel	0.1 g	–	–	–

Samples extracted for 24 h for each fraction.
All except (6) and (7) stirred at about 20°C.

Table 7

Solvent	Wt. Extract	Trans	Cis		Vinyl
MEK/Hexane = 5 : 1	0.35 g	8.4	90.9	0.7	
MEK/Hexane = 2 : 1	0.1 g	23.9	75.4	0.7	
MEK/Hexane = 1: 1	0.05 g	79.4	19.1	1.5	
Residue	0.28 g	96.3	2.9	0.8	

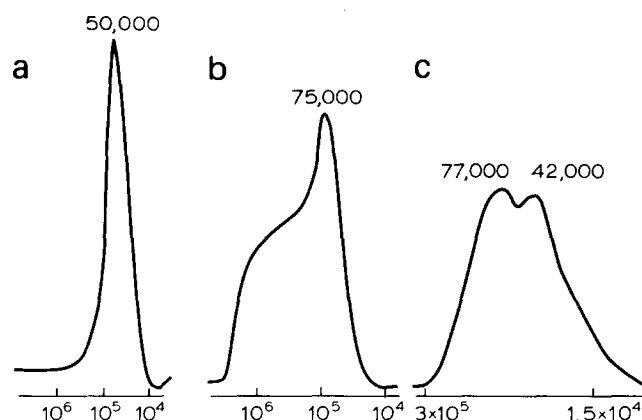Samples extracted for 24 h at 20°C

Figure 4 (a) 96% *trans* homopolymer: (b) Attempted block polymerization 73.0% trans. (c) Typical extracted fraction (toluene) 48.7% *trans*

spread of microstructure values may result from the broad spread of molecular weights normally observed with the rare earth high *cis* catalysts, although most of the fractions were plainly bimodal.

0.8 g of a synthetic mixture of *cis* polymer and *trans* polymer made with similar catalysts to the above and containing 51.6% *trans*/47.2% *cis*/1.2% vinyl was easily separated as shown in *Table 7*.

The mixture and the possible block polymer could be pressed into opaque sheets. The 'block' polymer showed some thermoplastic elastomer character and could be easily remoulded several times at 140°–150°C but tended to harden and discolour badly due to catalyst residues.

Table 8

	300% modulus	Tensile (MPa)	EAB
(1) 'Block' copolymer	3.85	7.30	413%
(2) Mixed homopolymers	2.49	3.68	457%

A brief test of physical properties gave the results shown in *Table 8*.

The ease of separation of mixed homopolymers confirms that the lack of separation of the possible block copolymer is not due to solubilization of the *trans* polymer by the *cis*. However, it is quite possible that in a mixture of homopolymers and block polymer, the block polymer would help to solubilize the *trans*. The limited evidence obtained so far is consistent with the latter situation.

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