Sequential formation of *trans* and *cis* butadiene homopolymers with one catalyst system

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When butadiene is polymerized in dichloroethane using dibutyl magnesium plus neodymium versatate as catalyst, high-*trans* polymer is formed during the first few hours of polymerization, followed by slow polymerization of the remaining butadiene to high-*cis* polymer after 7–8 h. This change probably occurs as a result of slow reaction between catalyst and solvent.

(Keywords: butadiene; rare earth; dichloroethane)

Introduction

It has been reported in previous papers[1,2] that catalysts consisting of dibutyl magnesium and mixed rare earth ('didymium') versatates produce high-*trans* polybutadiene in hexane solvent, while the addition of alkyl aluminium halides to the same catalysts results in the formation of high-*cis* polymer. In these early experiments the ratio of Mg to rare earth required for high polymerization activity appeared to lie in a very narrow range, from about 8:1 to 12:1, with a maximum monomer conversion of 65–70%. Subsequent work has shown that with neodymium versatate, activity increases steadily with increase in Mg:Nd ratio such that at 20:1, 80% and 90% conversion can be obtained with [Nd] = 0.26 and 0.39 mM per 100 g butadiene, respectively. Other workers have shown that it is possible to polymerize styrene[3] and copolymerize butadiene and styrene[4] using soluble or supported catalysts[5,6] comprising alkyl aluminiums, neodymium salts and relatively unreactive halides such as $CHCl_3$ or CCl_4.

The present work, using organic halides as solvent, was undertaken (a) with a view to further improving butadiene conversion by using a more polar but non-coordinating solvent, and (b) to explore the possibility of styrene–butadiene copolymerization. Both of these aims proved unsuccessful but led to a novel type of butadiene polymerization.

General details of polymerization, analyses and evaluation are to be found in refs 1, 2 and 7. Dichloroethane was redistilled twice from fresh calcium oxide. Molecular weight (*MW*) of the polymers was calculated approximately using the Mark–Houwink equation with K and a constants appropriate to *trans* polybutadiene, since the interest was in the shape of the distribution rather than absolute values.

Butadiene (Bd) was polymerized in 1,2-dichloroethane (DCE) for 5 h at 60°C and bottles were allowed to cool overnight (total 22 h) to 20°C before the polymer was isolated. The polymer cement (polymer + solvent) was rubbery and sticky and obviously not high-*trans* polymer. Although *cis* contents were approximately 30–50%, the dried material did not have the appearance of a polymer with random *cis–trans* microstructure of this *cis* level, being hard, tough and opaque. Viscosity, appearance and physical behaviour suggested a mixture of high-*cis* and high-*trans* polymers, and this was confirmed by the shape of qualitative g.p.c. traces which showed high *MW* (600 000–900 000) broad peaks typical of *cis* polybutadiene, plus very low *MW* (50 000–80 000) narrow peaks, similar to those of *trans* polymer produced with the same catalyst in hexane. The ratio of the area of these peaks was similar to the *cis*/*trans* ratio from microstructure determination.

In order to establish the stage at which *cis* polymer started to form, identical bottle polymerizations were carried out for various times up to 24 h in DCE. Microstructure and conversion *versus* time were measured. One set of polymerizations was run and sampled at intervals over 14 h and a second set was run overnight for 14 h and then sampled over the next 15–24 h. The results in *Table 1* show the onset of

Table 1 Butadiene polymerization at 60°C in dichloroethane

Time (h)	Conversion (%)	Inherent viscosity	*Trans* (%)	*Cis* (%)	Vinyl (%)
2	42.2	0.53	97.8	0	2.2
3	48.1	0.59	98.3	0	1.7
4	57.5	0.68	97.2	0	2.8
6	59.8	0.76	97.9	0	2.1
7	64.3	0.81	97.7	0	2.3
8	64.3	0.93	95.9	1.9	2.2
9	66.7	1.05	94.8	3.2	2.0
10	70.1	1.61	84.4	13.6	2.0
12	75.0	1.74	80.8	16.5	2.7
14	77.3	2.23	79.4	18.3	2.3
15	66.5	1.76	90.0	8.7	1.3
16	71.1	1.52	84.4	13.1	2.5
17	74.2	1.88	88.3	9.9	1.8
18	82.2	1.51	89.2	8.9	1.9
19	74.5	1.41	88.6	10.0	1.4
20	76.5	1.37	84.2	13.5	2.3
21	83.2	1.43	85.4	12.6	2.0
22	80.3	1.45	77.0	20.1	2.9
23	76.4	1.54	81.7	16.0	2.3
24	80.8	1.43	85.5	12.2	2.3

[Nd] = 0.26 mM/100 g Bd. Molar ratio Mg:Nd = 14:1

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cis homopolymer formation after about 8 h, after *trans* homopolymer formation had practically ceased, followed by very slow *cis* polymerization. The scatter in the results seems to be characteristic of polymerizations in chlorinated solvent and may be due to the effect of the latter on the nitrile rubber bottle seals over an extended period.

To increase polymerization rate and thus reduce contact time between solvent vapour and bottle seals, the neodymium concentration was increased. This resulted in more rapid *trans* polymerization to higher conversion (85%) leaving less free monomer for further conversion to *cis* polymer. However, *cis* homopolymerization still started after about 8 h.

Data collected from these and other experiments suggest that the amount of *cis* polymer formed depends on the final conversion to *trans* in the first stage. Thus increased Mg:Nd ratio results in improved *trans* polymerization at the expense of *cis*, and an increase in catalyst level at a given ratio also has the same effect. On occasions when *trans* polymerization has been poor for unknown reasons, *cis* contents up to 50% have been obtained.

Sequential polymerization of butadiene to high-*trans* and high-*cis* polymer can also be carried out in hexane using a three-component catalyst comprising Bu_2Mg, NdV_3 and ^tBuCl. The product had a maximum *cis* content of 46% at 53% overall conversion using a molar ratio of 14:1:3 and $[Nd]=0.26$ mM/100 g Bd. The same catalyst used in DCE gives a higher final percentage of *cis* polymer than the catalyst without ^tBuCl present, at the equivalent catalyst level. G.p.c. traces of polymers prepared in hexane with the three-component catalyst showed broad high *MW* peaks and narrow low *MW* peaks similar to those obtained from polymers prepared in dichloroethane with the two-component catalyst.

It has been shown[2] that a catalyst consisting of Bu_2Mg and NdV_3 modified by the addition of the highly reactive halide $AlEt_2Cl$, polymerizes butadiene in hexane solvent to give over 97% *cis* content in the final polymer. The polymer cement is always pale yellow and cloudy, the latter possibly due to formation of insoluble $MgCl_2$. The Bu_2Mg/NdV_3 catalyst in the absence of halide gives a clear, bright-yellow solution during *trans* polymerization in both hexane and DCE, but in DCE the solution becomes much paler yellow and less clear as *cis* polymerization takes over. Thus there seems little doubt that the switch in microstructure from *trans* to *cis* is the result of very slow reaction between the catalyst components and the chlorinated solvent. This latter effect would be similar to that found in conventional aluminium alkyl/neodymium salt/halide catalysts, where polymerization of butadiene to high-*cis* polymer is extremely slow if a primary organic halide is used instead of a tertiary halide or aluminium alkyl halide.

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