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HIGH *CIS*-1,4 POLYBUTADIENE—II

THE EFFECT OF IMPURITIES AND ADDITIVES ON THE CATALYST SYSTEM NICKEL DI*ISO*PROPYLSALICYLATE–BORON TRIFLUORIDE ETHERATE–LITHIUM BUTYL

E. W. Duck, D. K. Jenkins, D. P. Grieve and M. N. Thornber

Research and Development Laboratories, The International Synthetic Rubber Co. Ltd.,
Southampton

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Abstract—A description is given of the behaviour of the catalyst for high *cis*-1,4-polybutadiene (nickel di*iso*propylsalicylate–boron trifluoride etherate–lithium butyl) in the presence of 1,2-butadiene, methyl acetylene, 1-butene and various organic nitro compounds.

INTRODUCTION

One of the major factors involved in the production of a commercially acceptable polymer is control of molecular weight. In the rubber industry, in particular, the Mooney viscosity (a measure of plasticity and indirectly related to molecular weight) is used as an indication of processability, values between 60 and 100 giving favourable characteristics. Other factors which influence Mooney viscosity are chain branching, microstructure, crystallinity and copolymer constituents.

For polymers prepared with the same catalyst and with the same microstructure, Mooney viscosity is controlled by changes in molecular weight or molecular weight distribution. In simple anionic polymerization of butadiene by lithium alkyl, molecular weight in the absence of impurities is governed by catalyst concentration since one polymer chain should be initiated by each lithium alkyl molecule. Impurities such as 1,2-butadiene, oxygen, carbonyl compounds, acetylenes, water, etc., are known(1) to affect chain growth in such polymerizations by chain transfer, chain termination or destruction of active catalyst prior to polymerization. The situation for high *cis* polybutadiene is somewhat different. For the catalyst system nickel di*iso*propylsalicylate–boron trifluoride etherate–lithium butyl described in Part I(2) of this paper, molecular weights were not dependent on overall catalyst concentration although there was a variation with change in ratio of the catalyst constituents. Various patents(3) have described the use of compounds such as butenes, allenes and acetylenes to increase the processability of high *cis* polybutadienes prepared with catalysts which gave too high a molecular weight in the absence of suitable modifiers. The nickel di*iso*propylsalicylate catalyst gave polymers with good processing properties without modification but, since the commercial butadienes in use contained variable allene and acetylene contents, it was essential to determine the individual quantitative effects of these impurities in order to produce predictable Mooney viscosities in the final polymer.

The low Mooney viscosities produced when allenes were present in monomer feed streams to the extent of 1000 ppm prompted us to look for further additives which would increase molecular weight of the polymer in the presence of allenes. In a survey of compounds with this in mind, aliphatic nitro compounds were found to be partially effective.

EXPERIMENTAL

Catalyst preparation, polymerization and techniques employed were described in Part I.(2)

Methyl acetylene (Matheson) and butene-1 (Phillips Petroleum Co.) were dried by passage through 80 cm × 3 cm dia. columns of 3 Å molecular sieve. 1,2-butadiene was redistilled until 99·5 per cent pure by G.L.C. and stored over molecular sieve.

Aliphatic nitro compounds (Honeywill & Stein Ltd) and nitrobenzene (B.D.H.) were distilled from calcium hydride under dry nitrogen.

Hoekstra plasticity(4) was measured on a Bleeker–Hoekstra steam plastometer (Nederlandsche Optiek-en Instrumentenfabriek). A sample of rubber was pressed between parallel plattens at 100° for 30 sec under a load of 10 kg/cm.^{2} The percentage difference between initial and final thickness is the Hoekstra plasticity. (For high *cis* polybutadienes, Hoekstra plasticity was approximately 50 per cent of the Mooney viscosity).

Hoekstra (or Wallace Rapid Plasticity) measurements were used where:

(a) Limited amounts of sample were available.
(b) Large numbers of results were required quickly. Samples were milled to about 1 mm thickness, therefore temperature was attained rapidly and rapid determinations could be made.
This method of measurement is not suitable for rubbers of low plasticity (Hoekstra close to 100).

Where large samples (~ 20 g) were available, Mooney viscosities were measured using a shearing disc plastometer at 100°. The designation of the viscosity, ML_{1+4}, is given as Mooney measurement (M), large rotor used (L = large, S = small) and 1 + 4 indicates one minute warm up time and 4 minutes as the time of measurement after starting the rotor.

The relationship between Mooney and Hoekstra for the high *cis* polybutadiene polymers described in this paper is shown in Fig. 1.

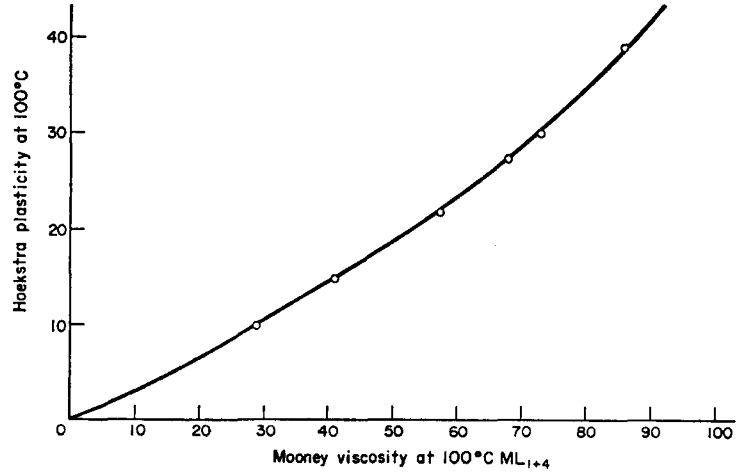


FIG. 1. Mooney viscosity vs. Hoekstra plasticity for high *cis* polybutadiene.

Determination of active lithium during scavenger level experiments was carried out by an adaptation of the Gilman Colour Test No. 1. Bottles of butadiene mixed feed were treated with varying levels of lithium butyl followed by a benzene solution of Michler's Ketone. After hydrolysis, colour was developed by adding iodine in glacial acetic acid, and examined spectrophotometrically.

RESULTS

(1) *Impurity effects*

The major impurities remaining in commercial 1,3-butadiene monomer after passage through molecular sieve, KOH/soda asbestos, and deoxygenating columns are butenes, acetylenes and 1,2-butadiene (methyl allene). Butadiene from manufacturer A contained an average of 250 ppm acetylenes and up to 50 ppm 1,2-butadiene, while butadiene from manufacturer B contained up to 1200 ppm 1,2-butadiene and less than 50 ppm acetylenes.

For lithium butyl polymerizations in these laboratories, a predetermined quantity of lithium butyl was added to the butadiene–solvent mixed feed to scavenge impurities (a quantity referred to as "catalyst demand"). The optimum catalyst demand level was determined by adding aliquots of lithium butyl solution to butadiene–solvent to find (a) the level at which Li—C bonds were not destroyed (Gilman colour test) or (b) the lowest level at which polymerization occurred. It was found that butadiene A had a high catalyst demand (0·025–0·03 parts catalyst per hundred monomer) since the reaction of lithium butyl with acetylenes was rapid and consumed more than one lithium butyl molecule per acetylene.(5,6) Butadiene B had a low catalyst demand (0·006–0·012 phm) because the reaction of lithium butyl with 1,2-butadiene was very slow(6) compared to the analysis time. This slow reaction meant that even scavenged samples of mixed feed still contained a high proportion of the original 1,2-butadiene.

1,2-*Butadiene*. 1,2-butadiene was synthesized in a 3-step reaction from crotyl bromide(7) and purified to give a single component (G.L.C. purity 99·5 per cent). For the polymerizations, Phillips High Purity butadiene containing less than 25 ppm 1,2-butadiene (G.L.C. analysis) was used. Polymerizations were carried out under the conditions described in Part I using a 20 per cent butadiene–hexane mixed feed to which known quantities of 1,2-butadiene were added prior to the catalyst. The results, using an active lithium butyl concentration of 0·09 phm and nickel di*iso*propylsalicylate:boron trifluoride etherate:lithium butyl ratio of 0·1:1·0:1·0 at 32°, are summarized in Table 1. Both conversion and Hoekstra Plasticity decrease with increasing 1,2-butadiene content although conversion is not affected by less than about 550 ppm. Polymer microstructure remained constant throughout at 95–97 per cent *cis*-1,4.

TABLE 1

1,2-Butadiene on 1,3-butadiene (ppm)	Hoekstra Plasticity	Conversion (%)	Approx. induction period
0	34	99	10 min
50	31	94	—
100	27	96·5	1 hr
250	20	98·0	3 hr
500	20	98·5	5 hr
950	18	79·5	—
1400	17	64·5	12 hr
1600	18	45·0	—

The most remarkable feature of the polymerizations was that, although the reaction was slower, the polymerizations with 1,2-butadiene present had considerable induction periods as shown in Fig. 2. Further measurements, omitted from the Fig. for clarity, indicated that the length of the induction period was roughly proportional to 1,2-butadiene concentration. [The actual times are only approximate as they represent the time taken to form 1–2 g polymer.] Similar experiments where aluminium triethyl was used in place of lithium butyl, at the same Ni : BF_3 : Al ratio and concentration, showed a similar but much less pronounced induction—30 min at 50 ppm 1,2-Bd, 1 hr at 500 ppm, 1½ hr at 900 ppm and 2 hr at 1400 ppm.

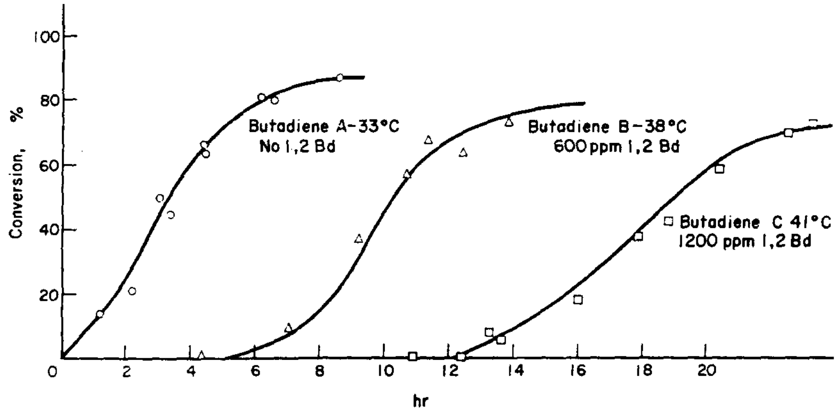


FIG. 2. Polymerization of commercial butadiene
Active BuLi = 0·135 phm.
Ni/BF_3 = 0·1 Li/BF_3 = 1·0.

TABLE 2

Me acetylene on 1,3 butadiene (ppm)	Temp. (°C)	Conversion (%)	Mooney viscosity	Time (hr)	Induction period (hr)
0	25	96	82	5	0
0	25	93	83	5	0
10	25	97	85	5	0
30	25	93	83	5	0
90	25	91	76	6	½
150	25	96	78	7	1
300	25	96	78,	7	1
500	25	98	77	7	1½
0	32	98	50	2½	0
30	32	91	46	2½	0
50	32	97	47	2½	0
100	32	95	47	3	½
150	32	96	46	3	½
300	32	90	43	3	1
400	32	94	42	5	2
500	32	95	42	5	2

Ni/BF_3 = 0·1 Li/BF_3 = 1·0 LiBu = 0·09 phm.

Methyl acetylene. Table 2 shows the results obtained by adding methyl acetylene to a hexane–high purity butadiene mixed feed prior to the catalyst.

The effect of methyl acetylene is similar to that of 1,2-butadiene but on a very much reduced scale. Conversion is unaffected up to 500 ppm, Mooney viscosity (almost a direct relationship with Hoekstra Plasticity for similar microstructures) shows a definite decrease but the induction period of 1½–2 hr at 500 ppm is much less than the 6 hr induction period for 1,2-butadiene at 600 ppm.

Butene-1. The results in Table 3 for butene-1 dosed into a normal high *cis* polymerization show that conversion was reduced at the higher levels of butene-1 addition; there was no change in *cis* configuration and I.V. did not change within experimental error.

TABLE 3

Butene-1 as % of Bd	BuLi *(phm)	Time (hr)	Conversion (%)	I.V.	% *cis*	% *trans*	% vinyl
0	0·08	8	96	2·4	96·6	2·0	1·4
0·3	0·08	8	94	2·5	97·1	1·6	1·3
0·8	0·08	8	93	2·5	96·8	1·9	1·3
1·2	0·08	8	88	2·5	96·8	2·0	1·2
0	0·22	5	92	2·2	96·4	2·0	1·6
0·4	0·22	5	96	2·2	96·5	1·9	1·6
0·8	0·22	5	90	2·2	96·0	2·2	1·8
1·2	0·22	5	88	2·2	96·5	2·1	1·4
2·8	0·22	5	83	2·2	96·2	2·2	1·6

*Parts per hundred of monomer.

Polymerization Temperature = 25°.
Ni : BF$_3$ = 0·1 : 1   Li : BF$_3$ = 1:1.

(2) *Addition of nitro compounds*

Nitromethane. Experiments carried out with Phillips High Purity butadiene at 33° showed that the rate of polymerization decreased as the nitromethane concentration increased but there was no increase in the normal polymerization induction period of approximately 15 min. When nitromethane was present in the range of nickel to nitromethane ratios 1:10 to 1:40, an increase in Mooney viscosity from 50 (for the control experiment with no nitromethane) to a maximum of 65 was observed. When the Ni:MeNO$_2$ ratio was increased beyond 1:40, the Mooney viscosity began to fall, until at 1:60 it was less than for the control experiment and at 1:100 was down to 32. The Mooney fall off was accompanied by a decrease in conversion. At 16°, a similar pattern of behaviour was apparent but the effective Ni:MeNO$_2$ ratio was 1:5 to 1:20, giving a Mooney increase from 80 to 100 at 1:5. Above 1:20, Mooney viscosity dropped more sharply with increase in Ni:MeNO$_2$ ratio than at 33°.

In all the experiments with nitro compounds, it was essential to add the modifier after the other three components and butadiene had been premixed. If nitromethane was added at any other stage in catalyst preparation, a white precipitate formed when lithium butyl came into contact with it, and no catalytic activity was observed. When the catalyst was allowed to form in the presence of butadiene before nitromethane addition, the characteristic yellow colour of the active catalyst developed and was not destroyed by addition of nitromethane.

When ordinary lithium butyl polymerization of butadiene was attempted in the presence of nitromethane, a flocculent white precipitate formed and no polymerization activity occurred with any order of addition or Li:$MeNO_2$ ratio.

TABLE 4

Temp. (°C)	Ni to $MeNO_2$ ratio	Conversion (%)	Mooney viscosity (ML_{1+4})	$MeNO_2$ conc. (phm)
33	0	99·0	53	0
33	1:0·5	96·5	50	0·004
33	1:1	96·0	58	0·009
33	1:2	98·0	57	0·017
33	1:5	96·5	59	0·043
33	1:10	98·0	67	0·086
33	1:20	92·5	72	0·172
33	1:30	94·0	71	0·258
33	1:40	77·0	60	0·344
33	1:50	61·5	43	0·430
33	1:100	38·0	31	0·860
16	0	100	79	—
16	1:5	100	98	0·043
16	1:20	99·0	90·0	0·172
16	1:30	98·0	72	0·258
16	1:40	90·8	55	0·344
16	1:50	92·0	37	0·430

NiDIPS : BF_3Et_2O : LiBu ratio = 0·1 : 1 : 1. Active LiBu = 0·09 phm.

In the presence of 1,2 butadiene up to 1600 ppm and with a polymerization temperature of 33°, the addition of nitromethane did not cause an increase in Mooney viscosity. Up to 400 ppm 1,2 Bd. at a 1:20 Ni/$MeNO_2$ ratio, the Mooney viscosity was maintained at the same level as the control without added nitromethane but, with increasing amounts of 1,2 butadiene, Mooney viscosity decreased and the previously mentioned induction period for polymerization increased exactly as for polymerization in the absence of nitromethane.

Other nitro compounds. Of the other nitro compounds investigated, only 1-nitropropane and nitroethane effected any useful change in the polymer properties. Polymerization in the presence of 1-nitropropane at Ni:nitropropane ratios from 1:5 to 1:100 showed a maximum rise of 15 in the Mooney viscosity but without such a large reduction in conversion as with nitromethane.

Nitroethane showed a similar but less marked trend, increasing the Mooney viscosity by 10 at Ni:$EtNO_2$ ratios of 1:60 to 1:70. The experimental results are recorded in Table 5.

2-nitropropane, nitrobenzene and *iso*amyl nitrate had no discernible effects on polymerization but no polymerization occurred in the presence of *iso*amyl nitrite.

TABLE 5

Nitro compound	Conc. in phm	Ni : nitro compound ratio	Conversion (%)	Mooney viscosity ML_{1+4}
1-Nitropropane	0	0	91	50
1-Nitropropane	0·053	1:5	90	53·5
1-Nitropropane	0·106	1:10	89	54·5
1-Nitropropane	0·212	1:20	89	57·5
1-Nitropropane	0·318	1:30	91	60·5
1-Nitropropane	0·424	1:40	90	64·5
1-Nitropropane	1·06	1:100	84	65·5
Nitroethane	0	0	98·5	59
Nitroethane	0·063	1:5	98·5	62
Nitroethane	0·126	1:10	99·0	64·5
Nitroethane	0·252	1:20	98·0	61·0
Nitroethane	0·377	1:30	98·0	61·0
Nitroethane	0·629	1:50	96·5	59·0
Nitroethane	1·50	1:120	91	51·0

NiDIPS : BF_3Et_2O : LiBu = 0·1 : 1·0 : 1·0.
Active LiBu = 0·09 phm.

DISCUSSION

Considering the effect of 1,2-butadiene on the catalyst nickel di*iso*propylsalicylate boron trifluoride etherate–lithium butyl, the only separate component known to react under mild conditions with 1,2-butadiene is lithium butyl itself. The reaction product of lithium butyl and boron trifluoride etherate,(8) namely lithium tetrabutyl borate, does not initiate butadiene polymerization and is therefore unlikely to metallate 1,2 butadiene. The known reaction of lithium butyl with 1,2-butadiene(6) is slow (256 hr to completion) and leads to 3-methylpropynylenedilithium associated with one mole of lithium butyl. Adams *et al.*(1) found that similar complexes prepared directly from 1-butyne and 1 : 1, 1 : 2 and 1 : 3 mixtures with lithium butyl gave respectively no polymer, polymer at a slower rate than lithium butyl, polymer at an even slower rate, when used to polymerize butadiene.

From a plot of number of lithium atoms against number average molecular weight, it was suggested that 3-methylpropynylenedilithium–lithium butyl produced high molecular weight polymer via a multicentre catalyst; no mention was made of an induction period.

The molecular weight of polybutadiene prepared with the high *cis* catalyst did not vary in a simple manner either with lithium butyl concentration or total catalyst concentration and it was not therefore possible to plot [Li] v. $\bar{M}_n$. If significant reaction between 1,2 butadiene and lithium butyl takes place (this is very unlikely since the polymerization was complete in 1/16 of the time required for the 1,2 Bd–LiBu reaction even allowing a 12-hr induction period), one would expect a rapid polymerization at low 1,2 Bd concentration becoming slower at higher concentrations and ceasing at a 1 : 1 lithium butyl–1,2 Bd ratio. There should be no induction period because all the possible intermediate complexes appear to be active catalysts for butadiene to some extent. In addition the highest 1,2 butadiene concentration of 1100 ppm shown in Fig. 2, corresponding to a 1·05:1 molar ratio of LiBu:1,2 Bd, should form an inactive white precipitate, but in fact polymerization still reaches about 70 per cent conversion. The presence of 1,3-butadiene in excess should provide a competing reagent for lithium butyl, which would reduce the availability of lithium butyl for 1:1 complex formation with 1,2-butadiene but would make an induction period even less likely.

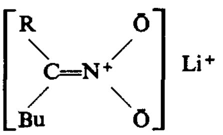
As reported earlier, nitromethane added to the complex 3 component catalyst, prepared in the presence of butadiene, caused no precipitation of lithium salt. This immediately suggests that no reactive lithium compound is present within about one minute of active catalyst formation. The major reaction of 1,2 butadiene must therefore be with the catalyst as a whole rather than an individual component. A somewhat analogous ethylene dimerization catalyst,(9) $Ni(PCl_3)_4$–$AlBr_3$–LiBu, will polymerize allene itself to crystalline vinylidene 1,2-polyallene. These facts suggest that the induction period could be due to slow polymerization of 1,2-butadiene, in preference to 1,3-butadiene, by the complex catalyst as a whole. At 1200 ppm, only 0·0012 g of poly 1,2-butadiene would be present in a 20–25 g sample of high *cis* polybutadiene and this would not affect the infra-red microstructure analysis appreciably. The smaller induction period for the aluminium triethyl based catalyst could result from a faster 1,2-butadiene polymerization since 1,3-butadiene polymerization is faster with aluminium triethyl than with lithium butyl. It would be surprising, nevertheless, that an allene could bond to a transition metal in preference to 1,3-butadiene co-ordinated in the *cis* configuration by two double bonds.

The effect of butene-1 on the polymerization (present as 0·4 per cent w/w) was small compared to 1,2 butadiene or methyl acetylene and experiments with this catalyst used in liquefied mixed butenes(10) showed that the maximum conversion decreased from about 80 per cent for a 46:54 volume–volume mixture of butadiene and butene-1 to 19 per cent for an 18:82 Bd–butene-1 mixture; the microstructure was only slightly affected, 94–95 per cent *cis* instead of 96–97 per cent; the I.V. was marginally lowered.

One of the problems associated with the manufacture of a high *cis* polybutadiene with the NiDIPS–BF_3Et_2O–LiBu catalyst was that the commercial butadiene in use for making linear low *cis* polymer contained up to 1000 ppm 1,2 butadiene. This, as shown in a previous section, causes a lowering of Mooney viscosity. In addition to this effect, the use of lithium butyl gave a lower Mooney viscosity than similar catalysts in which the lithium butyl was replaced by aluminium alkyl as the third component(11) used by the Japanese Bridgestone Company.

It has been claimed(12) in the Patent Literature that certain nitrocompounds increased the yield of ethylene–propylene copolymers formed with Ziegler catalysts. In a series of scanning experiments on the effect of nitromethane on a range of ethylene, ethylene–propylene and butadiene catalysts, it was found that nitromethane increased the molecular weight of high *cis* polybutadiene when it was added after the formation of the NiDIPS–BF_3 etherate–LiBu catalyst. Further work was carried out to determine whether the addition of a nitrocompound would increase the polymer molecular weight in the presence of 1,2 butadiene, but the experiments with nitromethane indicated that the normal effect of 1,2-butadiene overruled any other factor. Probably the effect of nitrocompounds is to co-ordinate with the product of the catalyst and butadiene monomer but the weakness of the nitro group as a donor to transition metals results in displacement or non co-ordination when stronger donors, such as 1,2-butadiene, are present.

The white precipitates formed when lithium butyl and nitro compound were mixed during catalyst preparation were probably simple salts. It was found that nitromethane, and 1- or 2-nitropropane formed 1 : 1 salts when reacted with lithium butyl, with the possible structure



2-nitropropane formed what appeared to be a stable 1 : 2 salt with lithium butyl but further work was curtailed when the dry 1 : 2 salt of 1-nitropropane exploded. Since no precipitates were formed when the nitro compounds were added as the last catalyst components, it must be assumed that all lithium present had already been consumed, either as lithium fluoride or a salt of di*iso*propylsalicylic acid, during catalyst formation from the initial three components.

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Résumé—On décrit le comportement du catalyseur (diisopropylsalicilate de nickel/trifluorure de base/butyllithium) dans la préparation de polybutadiène-1,4 à forte teneur en structure *cis* en présence de butadiène-1,2, de méthylacétylène, de butène-1 et de divers composés organiques nitrosés.

Sommario—Si descrive il comportamento del catalizzatore per elevato cis-1, 4-polibutadiene (diisopropilsalicilato di nichel/eterato di trifluoruro di boro/butile di litio) in presenza di 1,2-butadiene, metilacetilene, 1-butilene e vari notrocomposti organici.

Zusammenfassung—Das Verhalten des Katalysators für Polybutadien mit hohem *cis*-1,4 Gehalt (Nickel-di*iso*propylsalicylat/Bortrifluorid/Lithiumbutyl) bei Gegenwart von 1,2-Butadien, Methylacetylen, 1-Buten und verschiedenen organischen Nitroverbindungen wird beschrieben.