# A novel approach to the synthesis of high 1,4-telechelic polybutadienes by an anionic route

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Evidence is given that the presence of a sterically hindered Lewis acid during the anionic polymerization of butadiene in tetrahydrofuran results in a product with enhanced 1,4-content. Trimesityl boron was the Lewis acid principally employed and its influence allowed the 1,4-content to be raised to 50%. A relatively slow but competing proton abstraction reaction with the propagating polybutadienyl anion was, however, observed and alternative more specific additives are suggested.

**Keywords** Elastomer; polybutadiene; telechelic; anionic polymerization; trialkyl boron

## INTRODUCTION

Telechelic (terminally functional) polybutadienes of low molecular weight ($\sim 3000$) are becoming increasingly important commercially as precursors of networks of well defined dimensions. Such liquid rubbers are further required to be of high 1,4-structure so that subsequent crosslinking will yield a material possessing good elastomeric properties.

Liquid rubbers of this type are currently made by a free radical process[1], although this technique is not ideal. Initiation is by a functional radical, for example, hydroxy-terminated polybutadiene (HTPB) may be prepared using hydrogen peroxide/ferrous iron initiating systems[2]—difunctionality being generated by the dominance of radical termination by combination (equations 1 and 2).

$$HO\cdot + M \rightarrow HOM\cdot \xrightarrow{(n-1)M} HOM_n^{\cdot} \qquad (1)$$

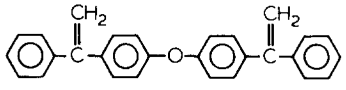
$$HOM_n^{\cdot} + HOM_m^{\cdot} \rightarrow HOM_{n+m}OH \qquad (2)$$

Although these materials possess the required high 1,4 structure ($\sim 80\%$), they have broad molecular weight distributions and, more importantly, are not uniquely difunctional as predicted by the above equations.

When butadiene is polymerized homogeneously to high conversion by a free radical process, the product is a mixture of a low molecular weight sol and a gel. This is caused by a low velocity of propagation[3] competing with a fast termination step[4] and a rapid attack on existing polymer chains[5]. Thus homogeneous free radical processes are used commercially only to prepare low molecular weight functionally terminated polymers, and even in these systems conversion is kept down to about 40% with minimal solvent present[1]. Despite these restrictions the product can exhibit significant branching and consequently yield an average molar functionality greater than 2, as demonstrated by the gelling which occurs on reaction of such HTPBs with diisocyanates.

Much more specifically difunctional material could, in principle, be prepared by living anionic processes were it not for the requirement that the structure should be high 1,4. It is well established that high 1,4-polybutadienes can be prepared anionically in inert hydrocarbon solvents by initiating with an alkyl lithium compound such as a butyl lithium. However, such initiators result in a polymer active at one end of the chain only, so that solely monofunctional polymers can be prepared in this way.

A great deal of effort has been expended to try to find dilithium initiators which are soluble in hydrocarbon solvents in order to create di-anionic polybutadienes capable of being converted into telechelic rubbers, but so far no clean straightforward system has been developed. Claims to have discovered one such system, involving *m*-diisopropenyl benzene and sec-butyl lithium[6,7], have been seriously challenged by other authors[8,9]. Tung *et al.*[10] have stated that the reaction of sec-butyl lithium with certain double 1,1-diphenyl ethylene compounds (I) does yield soluble difunctional adducts capable of acting as initiators and, very recently, Sigwalt[11] has described systems involving reaction of sec-butyl lithium with diolefines of structure typified by II.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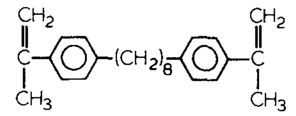
II

In these latter systems, however, the generation of the diadduct is very slow and, when formed, has to be solubilized by a seeding process. Even if these systems result in effective difunctional initiators, however, they all involve incorporation of catalyst units of appreciable size in relatively short chains, and this could well have a deleterious effect on the flexibility of the chains and consequently on the elastomeric properties of the subsequently crosslinked network.

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Butadiene may be polymerized anionically in polar solvents such as ethers in which difunctional initiators, and particularly electron transfer initiators, are soluble. The product, however, possesses only about 10% 1,4-structure[12] and therefore exhibits inferior elastomeric properties after crosslinking. The effect of such ethers on the polymer structure is dramatic; the addition of only minute amounts to a hydrocarbon solvent in which polybutadiene is being prepared anionically is sufficient to result in a polymer with predominantly vinylic structure[13].

In summary therefore, polybutadiene of high 1,4 structure may be prepared anionically in hydrocarbon solvents, but only by using monofunctional initiators since the common difunctional initiators are too polar to be soluble in these media. Difunctional initiators are soluble in ethers, but the use of such solvents results in polybutadienes of low 1,4 structure.

This communication reports on the use of sterically hindered Lewis acids as additives in the anionic polymerization of butadiene in the ether tetrahydrofuran (THF) in order to increase the 1,4 content of the resulting polymer. In this way the use of common difunctional anionic initiators to prepare telechelic high 1,4 content polybutadienes may be ultimately realized.

## EXPERIMENTAL

### *Materials*

Butadiene (Air Products) was dried by passing over molecular sieves and collected in a graduated vessel at −78°C.

Trimesityl boron (TMB) (Alfa) was recrystallized from benzene/methanol mixture, dried and stored under vacuum until use.

α-Methylstyrene (BDH) was dried over calcium hydride, then distilled under reduced pressure and the middle fraction collected (BP+26°C at 1 mm Hg).

Tetrahydrofuran (THF) (BDH), stabilized with 0.1% quinol, was distilled under nitrogen when required after sufficient 0.7 M sodium naphthalene solution in THF had been added to yield a permanent green colour.

n-butyllithium (Aldrich) was supplied and used directly as a 1.6 M solution in hexane.

Sodium metal (BDH), suppled as pellets under paraffin oil, was washed in 60–80 petroleum ether and pressed into 2 mm diameter wire for use.

### *General procedure*

Reactions were carried out in an atmosphere of nitrogen. Conventional Quickfit glassware was used which was subjected to the following cleansing procedure: It was heated to 400°C overnight in a muffle furnace, cooled to room temperature and washed with chromic acid, water (twice) and finally acetone. It was then dried and stored in an oven at 120°C until required.

Reagents were introduced by syringe through Subaseal serum caps (Gallenkamp). The syringes had been previously treated with the chromic acid cleansing procedure and had been stored at 120°C in the oven.

### *Polymerization of butadiene*

Three anionic initiators were employed: n-butyl lithium was used as supplied, whilst sodium naphthalene (NaN)[14] and the disodium tetramer of α-methylstyrene ($\alpha_4Na_2$)[15] were prepared by adaptations of well established routes.

A typical polymerization experiment was carried out as follows: A 500 ml round bottom 3-necked flask equipped with a magnetic follower, serum cap, bubbler for butadiene and a nitrogen inlet/outlet was used as a reaction vessel. 200 ml THF was introduced, as was 10 ml of butadiene out of 80 ml stored in an attached graduated flask. The appropriate amount of initiator solution was then injected and the solution allowed to polymerize for about 5 min, at which point a reference sample was removed and terminated with methanol and a solution of TMB in THF added to the remaining solution to achieve a calculated molar ratio of TMB to initiator. The remaining butadiene was then added and the solution left to polymerize for a further 30 min before termination with methanol. It was noted that the colour of the solution changed on addition of TMB from the yellow characteristic of the polybutadienyl anion to purple, and that the intensity of this colouration increased as reaction proceeded.

The sample and reference solutions were then reduced in volume by rotary evaporation, the polymers were precipitated from excess methanol and vacuum dried.

In some experiments the butadiene was added totally before addition of TMB, but the remaining procedures were carried out as described above.

### *Gel permeation chromatography (g.p.c.)*

Measurements were carried out on a Dupont series 870 chromatograph fitted with refractive index and u.v. detectors. Four styragel columns (Polymer Laboratories) of porosities $10^5$, $10^4$, $10^3$ and $10^2$ Å were used, and the molecular weights were determined from the retention times as polystyrene equivalents.

### *$^1H$ Nuclear magnetic resonance (n.m.r.) spectroscopy*

Measurements on small molecules were carried out principally on a Varian Associates EM60 60 MHz spectrometer on a Jeol PS100 100 MHz spectrometer. Polymer samples were analysed on a Jeol FX 90Q 90 MHz Fourier transform multiprobe spectrometer. Deuterochloroform was used as solvent with tetramethylsilane as reference.

### *Structural analysis*

Structural analyses of the polybutadiene samples for 1,4-content were carried out by $^1H$ n.m.r. spectroscopy. Analysis relied on the fact that the absorption centred at 5.3 δ was due to the tertiary hydrogens and to the double bond in both the 1,2 and the 1,4 structures, and that the absorption centred at 5.0 δ was due to the methylene hydrogens and to the double bond in the 1,2 structure only[16]. Thus the percentage 1,4 content was given by the formula

$$\frac{(A-\frac{1}{2}B)\times 100}{(A+\frac{1}{2}B)}$$

where A and B are the total integrated areas of the bands at 5.3 δ and 5.0 δ respectively.

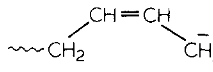
## RESULTS AND DISCUSSION

In order to consider ways by which the structures of polybutadienes prepared anionically may be controlled, it is necessary to appreciate the factors which determine the mode of monomer addition and, in particular, the role of the solvent.

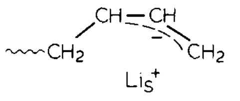
Ionic species may exist in solution in a number of forms, and some of these are represented schematically in equation 3 (where Me = metal ligand and S = solvent). These structures range from covalent aggregates on the LHS

$$\underset{(a)}{(\mathrm{R\ Me})_n} \rightleftharpoons \underset{(b)}{\mathrm{R\ Me}} \rightleftharpoons \underset{(c)}{\mathrm{R^-\ Me^+}} \rightleftharpoons \underset{(d)}{\mathrm{R^-\ S\ Me^+}} \rightleftharpoons \underset{(e)}{\mathrm{R^-\ \ldots\ Me^+}} \qquad (3)$$

through to free ions on the RHS, and the position of the overall equilibrium is critically dependent on the solvent. In inert solvents such as hydrocarbons the equilibrium lies well over to the left, with only the first three species being of significance. Of these, the contact ion pair, 3c, is the moiety by which polymerization occurs, and in butadiene systems this has been identified as the σ complex III, with a *cis–trans* ratio of about 3:1.



III



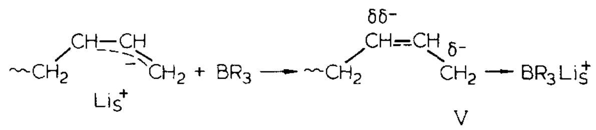
IV

Thus location of the negative charge on the terminal carbon ensures that, on addition of a further monomer, the terminal unit is incorporated into the chain in the 1,4 mode. Hence the high 1,4-structure observed in these solvents.

In solvating media the equilibrium lies to the right, the principal species present being the solvent separated ion pair, 3d. With butadiene as monomer this takes the form of the π-allyl complex IV, in which the electron densities at the 2- and 4-carbon atoms are comparable[18]. Thus the ingress of monomer results in enhanced possibility of reaction at the 2-carbon and the consequent increase in 1,2-addition. More detailed analysis of the effect of the form of the propagating end on the structure of the polymer has been carried out by Bywater[18].

If, therefore, a means were devised by which the propagating species in ethers were transformed from IV to III, then it is likely that the resulting polymer would possess increased 1,4-structure. Further, in such solvent systems difunctional initiators could then be used to produce telechelic materials.

Clearly, it is therefore required that the electron density in species IV be altered such that it lies predominantly on the 4-carbon atom, and this may be achieved in principle by interaction with an appropriate Lewis acid, such as a trialkyl boron (structure V, equation 4). The structure of the Lewis acid is important since interaction must be prevented from proceeding to reaction with the generation of the stable tetra alkyl boron salt[19]. The additive should therefore be sterically hindered, and a commercially available candidate known to fulfil this requirement is trimesityl boron (TMB) (VI)[20].



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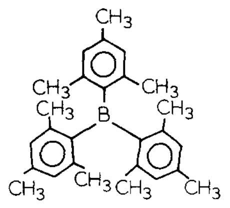
V



VI

Experiments were therefore carried out involving butadiene initiated in THF with a variety of anionic initiators. Only a short initial polymerization time of about 5 min was allowed before removal of a sample to be killed with methanol as a reference, and addition of a known quantity of TMB to the remaining propagating solution. After a further reaction time of about 30 min this system was also terminated, and the polymer and the reference material isolated. The polystyrene equivalent molecular weights of the sample and reference were then determined by g.p.c., and the structure of the polymers by $^1$H n.m.r. From this data the effect of TMB on the mode of butadiene addition was evaluated (for an assessment of the accuracy of this approach, see later).

*Figure 1* shows g.p.c. traces of the product and of the

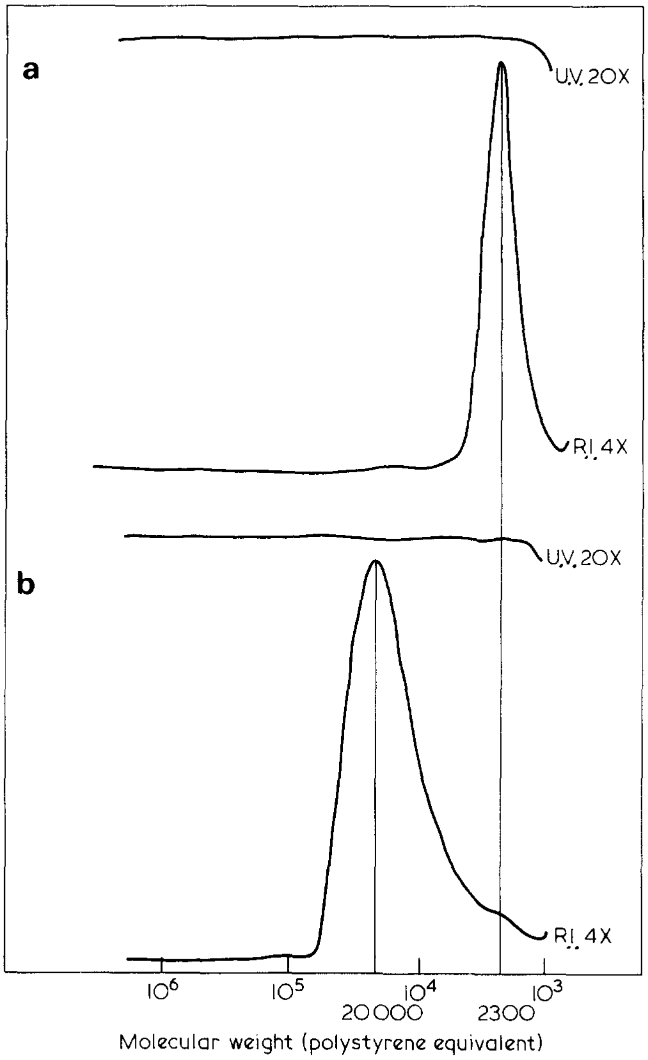


*Figure 1* G.p.c. traces of polybutadienes initiated with n-butyl lithium in THF at room temperature; (a) polybutadiene control terminated with methanol at time of addition of TMB to main sample, and (b) polybutadiene with TMB added 5 min after initiation and polymerized for a further 40 min before termination with methanol

*Table 1* Effect of TMB on the structure of polybutadiene anionically initiated in THF at 20°C

| Initiator | TMB: Living ends (molar ratio) | % 1,4 | % 1,2 |
|---|---|---|---|
| BuLi[1] | – | 9 | 91 |
| | 1 : 1 | 20 | 80 |
| | 2 : 1 | 25 | 75 |
| | 3 : 1 | 29 | 71 |
| $\alpha_4Na_2$[2] | – | 13 | 87 |
| | 1 : 1 | 25 | 75 |
| | 2 : 1 | 42 | 58 |
| | 3 : 1 | 51 | 49 |
| Na N[3] | – | 10 | 90 |
| | 1 : 1 | 29 | 71 |
| | 2 : 1 | 39 | 61 |
| | 3 : 1 | 47 | 53 |

[1] n-Butyl lithium
[2] Disodium salt of $\alpha$-methylstyrene tetramer
[3] Sodium naphthalene radical anion

control in a typical experiment, the peak maximum of the former corresponding to a polystyrene equivalent molecular weight very much greater than that of the latter. Polymerization has therefore continued in the presence of TMB although with some low molecular weight tailing. The tailing (for explanation, see later) results in a broadening of the molecular weight distribution of the product ($MWD = 1.6$) relative to the control ($MWD = 1.1$). Significantly, the product exhibits only low u.v. absorbance indicating that no appreciable tetra alkyl boron adduct has been formed. In contrast, when a non-sterically hindered Lewis acid, such as triphenylboron, is added *in lieu* of TMB, the g.p.c. of the products shows that polymerization is almost immediately terminated, and the material exhibits massive u.v. absorption corresponding to the adduct[19].

The structural data on the polymers produced in typical experiments are given in *Table 1*, where the conformations are evaluated for the portions of chains formed after the addition of TMB. Three anionic initiators were employed, and in all cases the effect of adding TMB was to increase the 1,4-content of the polymer. It is further seen that the 1,4-content increase is most marked when the counter ion employed is sodium; moreover in all three systems the 1,4-content increases with increasing molar ratio of TMB to living ends.

Lastly, *Table 2* demonstrates the effect of polymerization temperature on the structure of the polymer prepared via the living polymer/TMB complex, and it is apparent that the 1,4-content increases significantly as the temperature rises. This behaviour may be contrasted with the direct anionic polymerization of butadiene in hydrocarbon solvents where the polymer structure is virtually unaffected by changes in the temperature of polymerization over a wide range[21].

The method used for assessing the structural composition of that portion of the polybutadiene chain generated in the presence of TMB requires a knowledge of the ratio of the chain length grown under these conditions to the total chain length. Such an estimate was made from a comparison of the g.p.c. derived polystyrene equivalent molecular weights of the final product and of the control. Since, however, the control possesses a very low 1,4-structure and that of the product is very much higher, the accuracy of the estimate depends on the insensitivity of the proportionality between polystyrene equivalent molecular weight and that of polybutadiene to structural changes in the latter polymer.

The range of the error introduced by this approximation was assessed by using the values of K and $\alpha$ in the Mark–Houwink equation for high 1,2-polybutadiene and for high 1,4-polybutadiene[22], and relating them via Benoit's universal calibration ($[\eta]M = \text{constant}$). Such calculations revealed that the molecular weight of the product relative to the control could be overestimated by up to 8%. This could in turn lead to an underassessment of the 1,4-content of the polymer component, prepared in the presence of TMB, by up to the same figure, under the experimental conditions employed.

Since the molecular weights were determined from the peak retention times and the product invariably exhibited a low molecular weight tail, this would also lead to an underestimate of the 1,4-content of the TMB-influenced portion of the product. Thus the true effect of TMB on the structure is probably significantly greater than indicated by the data in *Tables 1* and *2*, and the conclusion must be drawn that the presence of TMB results in a substantial increase in the 1,4 content of polybutadiene.

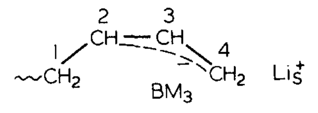
The direct dependence of 1,4-content on the relative amount of TMB added suggests that a dynamic equilibrium exists between the anion/TMB complex and its dissociated form; the former structure polymerizing butadiene primarily in the 1,4-mode and the latter primarily in the 1,2-mode. If this were so, then the introduction of increasing excess of TMB should lead to a product with a structure tending to that generated by the permanently complexed terminal group. This dependence has yet to be fully investigated, however, and the maximum 1,4-content recorded so far is 51%.

Evidence of complex formation could also be perhaps obtained from kinetic data, since it is reasonable to assume that the rate of propagation of the complexed form is less than that of the unassociated ion. Indeed there is some qualitative evidence that this is so; for example, in a typical experiment a polystyrene equivalent molecular weight of 6000 was achieved after 5 min in the absence of TMB, but this increased only to 14000 in the 30 min following its addition; there was sufficient monomer present to have produced chains of 30000 molecular weight. This kinetic effect is to be investigated further.

The detailed structure of the complex and the mechanism of its participation in the propagation process has also to be considered. As originally conceived above it was regarded as an interaction between the Lewis acid and the terminal carbon of the polymer chain (structure V) resulting in a distortion of the electron distribution to increase the charge density at the terminal carbon and thereby encourage monomer addition at that point.

*Table 2* Effect of temperature on the structure of polybutadiene anionically initiated by n-butyl lithium in THF in the presence of TMB (molar ratio TMB: living ends = 2 : 1)

| Temperature (°C) | % 1,4 | % 1,2 |
|---|---|---|
| –25 | 13 | 87 |
| 0 | 21 | 79 |
| 20 | 25 | 75 |
| 45 | 32 | 68 |

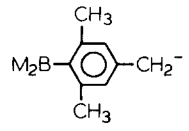


VII

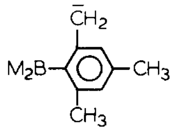
Alternatively, the complex can be visualized as being of structure VII in which the TMB is located in the position of the lithium ion in the $\pi$-allyl complex (IV) and the electron distribution of the terminal anion is virtually unaffected by its presence. The 1,4-directing polymerization mechanism of the complex would then result through steric hindrance in which the proximity of the bulky TMB molecule to the 2-carbon effectively blocks access of monomer to this point, and thereby allows addition to occur only at the more exposed terminal carbon. The relative contributions of these alternative models to the propagation transition state can only be assessed by further, more mechanistically orientated investigations.

A feature of all the reactions involving TMB is the gradual onset of an intense purple colouration ($\lambda_{max} = 505\,nm$) of the solution on its addition. This clearly indicates the presence of a side reaction involving TMB which is, however, not rapid enough to deactivate completely the propagating ends during the time scale of the experiment, although the low molecular weight tailing observed with the product could well be ascribed to this process.

The most probable reactions between the polybutadienyl anion and the TMB are addition and proton transfer. The former has already been discounted from g.p.c. evidence since it would result in substantial u.v. absorbance of the product and, in any case, tetraalkyl boron salts are generally colourless. Proton transfer would result in hydrogen termination of the polybutadienyl anion and the creation of a TMB anion (VIII a or b).



VIII a



VIII b

In either structure the anion is stabilized by benzylic resonance and by the electron withdrawing characteristics of the adjacent boron. Indeed, if formed, the resonance stabilization of the anion would have to be sufficiently great to prevent it initiating the polymerization of butadiene since this would lead to u.v. absorption in the product g.p.c. traces, and this is not observed.

Confirmation that the side reaction involved proton transfer was obtained when it was shown that an identical intense purple colouration was induced much more rapidly if n-butyl lithium was reacted with TMB under the same conditions. Such reactions were carried out with equimolar reagents and the system subsequently terminated with methyl iodide. The product was then isolated and analysed by $^1H$ n.m.r. The analytical data is given in *Table 3* which establishes that the product is uniquely (4-ethyl 2,6 dimethylphenyl) bis 2,4,6 (trimethylphenyl) boron, and that the anion must consequently have been of structure VIIIa. Other workers[23] have recently used dueteration techniques to show that the VIIIa anion is formed under circumstances similar to these.

*Table 3* $^1H$ n.m.r. analysis of product resulting from termination of the reaction between n-butyl lithium and TMB with methyl iodide. Product = [(4-ethyl, 2,6-dimethyl phenyl) bis-2,4,6 (trimethylphenyl)] boron

| Chemical shift ($\delta$) | Splitting | Relative area | Identity |
|---|---|---|---|
| 6.64 | singlet | 6 | Arom H |
| 2.60 | quadruplet | 2 | $-\underline{CH_2}-CH_3$ |
| 2.21 | singlet | 6 | *para* $CH_3$ |
| 1.97 | singlet | 18 | *ortho* $CH_3$ |
| 1.21 | triplet | 3 | $-CH_2-\underline{CH_3}$ |

Addition of butadiene to a solution of the TMB anion generated with n-butyl lithium did not result in any polymerization, confirming the inactivity of species VIIIa under these conditions.

Although this preliminary evidence, therefore, confirms that the presence of sterically hindered Lewis acids during the anionic polymerization of butadiene significantly increases the proportion of 1,4-structure in the product, TMB is not the ideal additive to perform this function. Firstly it is subject to a proton abstraction termination reaction which, albeit relatively slow, affects the molecular weight distribution of the product and ultimately, the efficiency of any functionalizing reaction which might subsequently be introduced. Secondly, it is very expensive and therefore not attractive in any commercial application without an efficient means of recovery.

A programme to synthesize other sterically hindered boron alkyls has therefore been initiated. Trinaphthyl boron seems a likely candidate, and tri(2,6-dimethylphenyl) boron has been prepared and subjected to a preliminary examination. The latter compound does not possess methyl groups at the vulnerable *para* positions, and should not therefore be so subject to proton abstraction as TMB. In fact, little if any abstraction takes place, and the 1,4-composition of the polybutadiene formed is nevertheless enhanced by its presence. Bulky Lewis acids based on other elements such as aluminium should also exhibit similar coordination and 1,4-enhancement, and such compounds will be sought and included in future investigations.

## REFERENCES

1 French, D. M. *Rubber Chem. Technol.* 1969, **42**, 71
2 Seligman, K. L. US Pat. 2877212 (March 10, 1959)
3 Morton, H., Salatellio, P. P. and Landfield, H. *J. Polym. Sci.* 1952, **8**, 815
4 Cooper, W. and Vaughan, G. 'Progress in Polymer Science', (Ed. A. D. Jenkins), Vol.1, Pergamon Press, 1967, p 93
5 Hayes, R. A. *J. Polym. Sci.* 1954, **13**, 583
6 Foss, R. P., Jacobson, H. W. and Sharkey, W. H. *Macromolecules* 1977, **10**, 287
7 Beinert, G., Lutz, P., Franta, R. and Rempp, P. *Makromol. Chem.* 1977, **179**, 551
8 Cameron, G. G. and Buchan, G. M. *Polymer* 1979, **20**, 1129
9 Fetters, L. J., Kamienski, C. W., Morrison, R. C. and Young, R. N. *Macromolecules* 1979, **12**, 344
10 Tung, L. H., Lo, G. Y-S. and Bayer, D. E. *Macromolecules* 1978, **11**, 616

11 Guyot, P., Favier, J. C., Uytterhoeven, H., Fontanille, M. and Sigwalt, P. *Polymer* 1981, **22**, 1724

12 Richards, D. H. *Chem. Soc. Rev.* 1977, **6**, 235

13 Duck, E. W. and Locke, M. *J. Inst. Rubber Ind.* (*A*) 1968, **6**, 3407

14 Burgess, F. J. *MSc Thesis* University of St Andrews (1976)

15 Richards, D. H. and Williams, R. L. *J. Polym. Sci., Polym. Chem. Edn.* 1973, **11**, 89

16 Chen, H. Y. *Anal. Chem.* 1962, **34**, 1134, 1793

17 Brownstein, S., Bywater, S. and Worsfold, D. J. *Macromolecules* 1973, **6**, 715

18 Bywater, S. 'Progress in Polymer Science', (Ed. A. D. Jenkins), Vol 4, Pergamon Press, 1975, p 27

19 Richards, D. H. and Stewart, M. J. Br. Pat. Appl. No. 8212032

20 Brown, H. C. and Dodson, V. H. *J. Am. Chem. Soc.* 1957, **79**, 2302

21 Kuntz, I. and Greber, A. *J. Polym. Sci.* 1960, **42**, 299

22 Kraus, G. and Stacy, C. J. *J. Polym. Sci. A2* 1972, **10**, 657

23 Ramsey, B. G. and Isabelle, L. M. *J. Org. Chem.* 1981, **46**, 179

24 Richards, D. H. and Stewart, M. J. Br. Pat. Appl. No. 8212033

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This work is the subject of a British patent application[24].