

# Efficiency of *n*-butyllithium/ *m*-diisopropenylbenzene diadduct as a dicarbanion initiator in the making of $\alpha,\omega$ -hydroxyl terminated polybutadiene using oxetane as the capping agent

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The diadduct made from a 2:1 ratio of *n*-butyllithium to *m*-diisopropenylbenzene has been evaluated as a diinitiator for synthesizing  $\alpha,\omega$ -hydroxyl terminated polybutadiene in cyclohexane solution. While the g.c./m.s. analysis results showed the predominant formation of the diadduct at 20°C, an incomplete reaction at 0°C led to a mixture containing a variety of initiating species of varying number of carbon–lithium ends. The observed narrow monomodal molecular weight distribution resulting from the use of this mixture indicated that this diadduct did not react as a diinitiator but rather as a monoinitiator. Although one of the two carbon–lithium ends of the diadduct was inactive during the polymerization, both ends were able to react with oxetane, thus forming the  $\alpha,\omega$ -hydroxyl terminated polybutadiene. This monofunctionality during polymerization and difunctionality towards the capping reaction has been corroborated by <sup>1</sup>H n.m.r., <sup>13</sup>C n.m.r. and hydroxyl titration. The capping reaction of the carbon–lithium end was as efficient for poly(butadienyl)dilithium, synthesized using the diadduct as the initiator, as for poly(butadienyl)lithium, synthesized using *n*-BuLi as the initiator. The inactivity of one of the two carbon–lithium ends during the polymerization did not prevent the diadduct from being an effective initiator for making telechelic HTPB.  
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(Keywords:  $\alpha,\omega$ -hydroxyl terminated polybutadiene; diinitiator; oxetane)

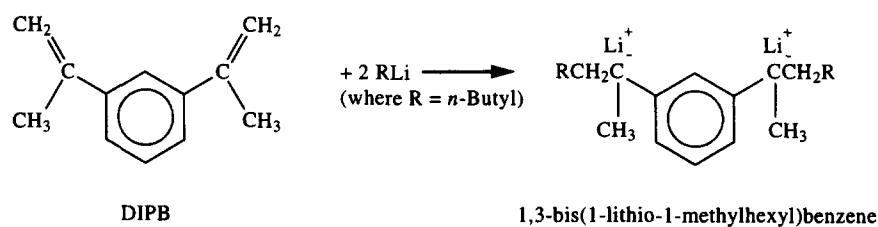
## INTRODUCTION

Interest in the anionic synthesis of well-defined triblock copolymers, such as ABA copolymers, by a two-step method, and telechelic polymers, such as  $\alpha,\omega$ -hydroxyl terminated polybutadiene (HTPB), has prompted diinitiator studies<sup>1–36</sup>. Among all the diinitiator studies, considerable portion was focused on the lithiation of *m*-diisopropenylbenzene (DIPB), using either *n*-butyllithium or *s*-butyllithium, due to the low ceiling temperature of DIPB for preventing homopolymerization and the good solubility of the formed diinitiator in hydrocarbon media. While the association of diinitiators and the addition of polar additives might affect a diinitiating process, as previously pointed out by Fetters *et al.*<sup>31</sup> and Quirk and Ma<sup>32</sup>, observations and conclusions on the efficiency of the formed diinitiator—1,3-bis(1-lithio-1-methylhexyl)benzene or 1,3-bis(1-lithio-1,3-dimethylpentyl)benzene—varied significantly among all researchers. Many researchers reported their lithiated DIPB was an efficient difunctional initiator. Beinert *et al.*<sup>18</sup> found the addition of two molecules of *sec*-butyllithium to one molecule of DIPB produced an

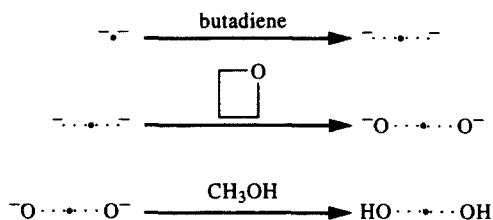
efficient bifunctional initiator soluble in non-polar solvents. Lutz *et al.*<sup>19</sup> reported that the butyllithium diadduct of diisopropenylbenzene, formed in benzene at temperatures ranging between 35°C and 52°C, was an efficient diinitiator in the absence of any polar additive. Foss *et al.*<sup>20</sup> obtained an efficient diinitiator with good solubility by the addition of 0.1 molecules of triethylamine per lithium site as the promoter and the subsequent attachment of 5 isoprene units per lithium site. Kamienski *et al.*<sup>28</sup> added equimolar quantities of triethylamine to *sec*-butyllithium and obtained quantitative yield of an efficient diinitiator with excellent stability. Ladd and Hogen-Esch<sup>33</sup> studied the lithiation of DIPB in benzene using *s*-BuLi, and synthesized a PMMA–PBD–PMMA triblock copolymer. On the other hand, different results were obtained by Cameron and Buchan<sup>29</sup> and Yu *et al.*<sup>34–36</sup>. The former claimed that the lithiation reaction led to a mixture of di- and polyfunctional initiators rather than to a diinitiator, whereas the latter presented their evaluation results showing their diadduct reacting as a monoinitiator in a hydrocarbon solvent even in the presence of triethylamine (TEA) at a 10/1 TEA/Li ratio. Researchers who obtained an efficient diinitiator often supported their conclusions by showing their g.p.c. analyses indicating a narrow and expected molecular weight of the formed copolymer, which in reality was not sufficient to

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Scheme 1



Scheme 2

distinguish a triblock copolymer from a diblock copolymer. Those who claimed no diinitiation have based their conclusions on the lack of mechanical properties of the formed copolymer and on the molecular weight of the remaining block after cleavage of the polybutadiene block.

In this paper, our findings on 1,3-bis(1-lithio-1-methylhexyl)benzene during the preparation of the  $\alpha,\omega$ -hydroxyl terminated polybutadiene are presented on the basis of evidence other than g.p.c. chromatograms and mechanical properties. The hydroxyl functional groups were generated by end-capping the living chain ends with oxetane, followed by methanol termination. This work involved (1) making the diinitiator and evaluating its efficiency of diinitiating via g.c./m.s. analysis, and (2) examining the oxetane capping reaction on the basis of n.m.r. spectra. The preparative method and the observed phenomena are discussed, along with the evaluation results.

## EXPERIMENTAL

### Materials

Butadiene and styrene used in this work were obtained from Taiwan Synthetic Rubber Corp. (TSRC) and pretreated with activated alumina (from Alcoa Co.) prior to their use. Cyclohexane was distilled, treated with activated alumina and degassed. THF, triethylamine and oxetane were purchased from Merck and pretreated with activated alumina and degassed. Reagent grade *m*-diisopropenylbenzene was purchased from TCI, treated with activated alumina and degassed. *n*-butyllithium was purchased from TCI as 15 wt% solution in hexane.

### Preparation of the diinitiator

The dicarbanion initiator used for the polymer synthesis in this work was prepared by reacting *n*-butyllithium with *m*-diisopropenylbenzene in *n*-hexane solvent. A required amount of *n*-butyllithium in hexane solution was charged and sealed into a glass bottle in an air-free glove box. Prescribed amounts of triethylamine and *n*-hexane were then added into the bottle, using syringes, to make a total 15 wt% solution.

This sealed bottle was kept with magnet stirring in an *n*-hexane bath at constant temperature. *m*-Diisopropenylbenzene was then added into the bottle in a dropwise manner and the solution turned red, indicating the formation of the diadduct. The extent of DIPB reaction was determined through a measurement of double bonds using FTi.r. The thus formed diadduct solution was stored in a refrigerator for later use. The mechanism of the formation of the diinitiator is shown in Scheme 1.

### Analysis of the diinitiator

The diinitiator was analysed using Finnigan MAT g.c./m.s. equipped with an ITD detector. This instrument has a DB-5 J&W capillary column of 30 m length and 0.32 mm diameter. The injection temperature was 280°C. After being kept at 80°C for 5 min, the column was heated at a rate of 6°C min<sup>-1</sup> to 280°C and maintained at that temperature for another 5 min.

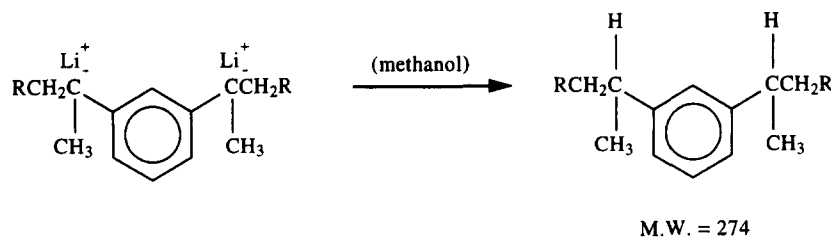
### HTPB synthesis using the diadduct

The synthesis of HTPB was accomplished in cyclohexane solvent. First, appropriate amounts of cyclohexane and THF were put into a 1 l pressure vessel under a slight nitrogen overpressure. The vessel content was then heated to a specified temperature prior to the addition of the required weight of the diinitiator. Afterwards the butadiene was charged and anionic polymerization occurred. Five minutes after the vessel temperature reached the maximum, the capping agent, oxetane, was charged into the vessel in 50% excess over the stoichiometric amount. The capping reaction was allowed to proceed for 6 h. The yellowish colour of the polybutadienyllithium ends disappeared after the capping. The living lithium oxide chain ends were then deactivated by the addition of methanol. For an efficient diinitiating process, the overall HTPB synthesis reaction should be as shown in Scheme 2, in which  $\cdot$  represents the aforementioned diadduct, 1,3-bis(1-lithio-1-methylhexyl)benzene.

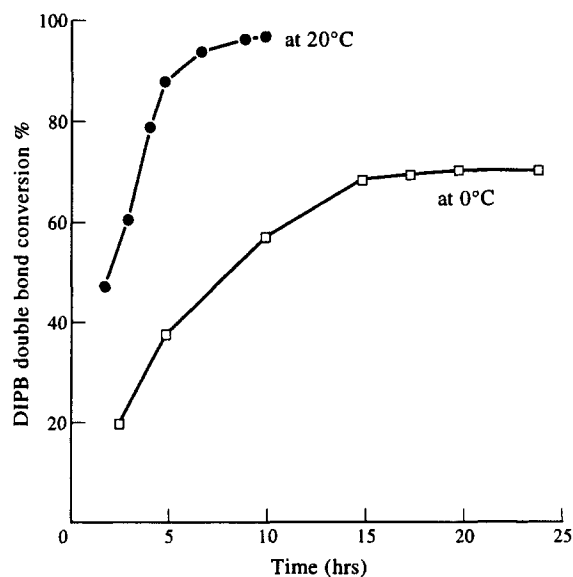
### Purification and analysis of the synthesized polymer

The thus formed HTPB solution was purified using a tenfold volume of 3 wt% HCl to wash out the residual lithium methoxide and TEA, followed by repeated washes with distilled water. The organic layer was separated from the aqueous layer and dried with a molecular sieve. The HTPB was finally precipitated as viscous oil in methanol and dried in a vacuum oven.

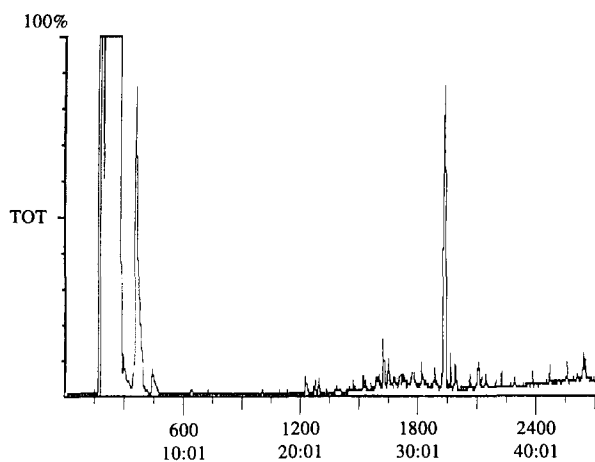
The molecular weights and molecular weight distributions of the synthesized polymers were determined by Waters gel permeation chromatography (g.p.c.) equipped with Waters M-486 adsorbance (u.v.) and Waters 410 differential refractive index (r.i.) detectors.



Scheme 3



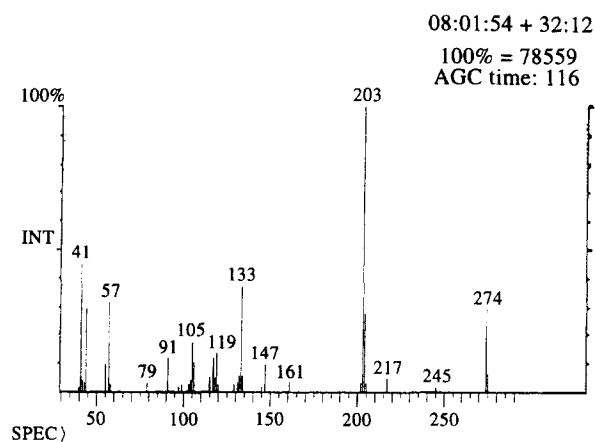
**Figure 1** Conversion of the double bonds of DIPB as a function of time (*n*-BuLi/DIPB=2, TEA/*n*-BuLi=0.8, in *n*-hexane)



**Figure 2** G.c. chromatogram of the initiating system formed at 20°C

The g.p.c. was typically operated using three Waters Ultrastaygel columns ( $10^3$ ,  $10^4$  and  $10^5$  Å) at a nominal flow rate of  $1 \text{ ml min}^{-1}$  with a sample concentration of 0.1% in THF solvent. For low molecular weight samples, the above column set was replaced with a PLgel 3U column manufactured by Polymer Lab, UK. The microstructure was determined by the Shimadzu FTIR-8101M spectrometer using a liquid  $\text{N}_2$ -cooled MCT detector. The spectral resolution was  $2 \text{ cm}^{-1}$ .

The total number of hydroxyl functional groups was determined from  $^1\text{H}$  n.m.r. and  $^{13}\text{C}$  n.m.r. spectra using



**Figure 3** M.s. spectrum of the g.c. peak at 32:12

a Bruker AMX400 100.61 MHz spectrometer at 25°C in  $\text{CDCl}_3$ . In the meantime, the total number of hydroxyl functional groups was also determined in accordance with the ASTM method E222-66B<sup>37</sup>. Acetic anhydride was added in excess to a pyridine solution containing the dissolved HTPB. The reaction was kept at reflux temperature for 90 min to ensure a complete esterification of the hydroxyls. The unreacted acetic anhydride was then hydrolysed by adding water and the resulting carboxyls were titrated by sodium hydroxide using phenolphthalein as the indicator. Analogous procedures were also done on a blank pyridine solution containing no HTPB. The difference between the titration results led directly to the number of hydroxyls originally contained in the HTPB.

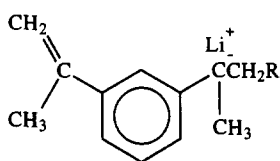
## RESULTS AND DISCUSSION

The reaction of two moles of *n*-BuLi with one mole of DIPB at a temperature of 20°C, in the presence of TEA at a TEA/*n*-BuLi ratio of 0.8, forms the 1,3-bis(1-lithio-1-methylhexyl)benzene diadduct, with a conversion of the double bonds of DIPB greater than 96% after 10 h, as illustrated in *Figure 1*. The conversion of the double bonds of DIPB was determined using FTIR spectra. The double bonds of the DIPB had a peak at  $890 \text{ cm}^{-1}$ . Their conversion was calculated by comparing the absorption peaks before and after the reaction, the intensities of both peaks being first normalized against the absorption peak of *meta*-substituted benzene at  $750\text{--}810 \text{ cm}^{-1}$ . The formation of this diadduct was verified through the existence of its hydrocarbon derivative after hydrolysis (*Scheme 3*).

Our g.c./m.s. confirmation of the molecular weight of this hydrocarbon derivative is shown in *Figures 2* and *3*. The peak in the g.c. chromatogram was identified, using

**Table 1** Comparison between two initiating systems formed using a 2/1 molar ratio of *n*-BuLi to DIPB at different temperatures (resulting in various DIPB double bond conversions)

	Using initiator formed at 20°C	Using initiator formed at 0°C
DIPB double bond conversion	complete	incomplete
initiating species	diadduct	mixture of <i>n</i> -BuLi, monoadduct, diadduct
mole ratio of TEA/ <i>n</i> -BuLi	0.8	0.8
solvent used for making initiators	<i>n</i> -hexane	<i>n</i> -hexane
initiator concentration	15 wt%	15 wt%
monomer	styrene	styrene
expected MW	30 000	30 000
g.p.c. $M_n$	30 858	23 093
g.p.c. $M_w$	34 091	26 658
polydispersity	1.10	1.15



Scheme 4

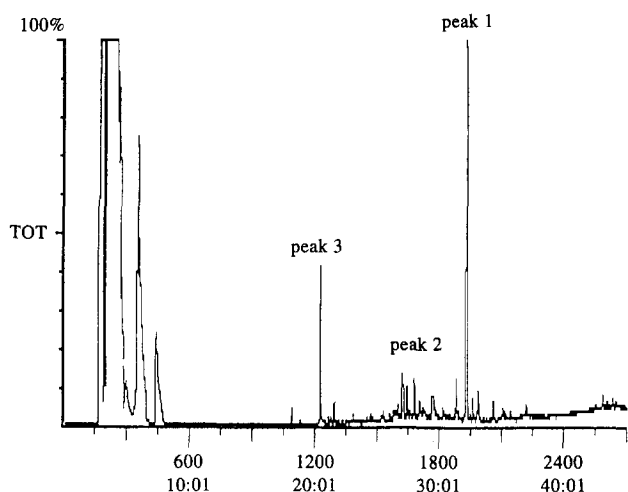
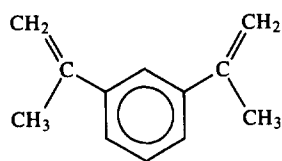


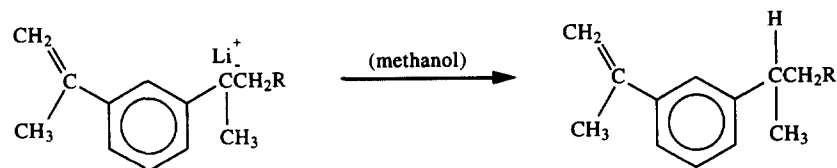
Figure 4 G.c. chromatogram of the initiating system formed at 0°C

the m.s. spectrometer, as the hydrocarbon derivative having a parent ion of  $m/e$  274. Other species shown at low  $m/e$  were the fragment ions of the parent ion. In contrast to our observations, Yu *et al.*<sup>35</sup> found that oligomerization occurred in early stages and a quasi-equilibrium between the diadduct and various oligomers existed when *sec*-butyllithium was added onto *m*-DIPB at 20°C in cyclohexane solvent. However, this quasi-equilibrium disappeared as the oligomers depolymerized when the reaction was conducted at 50°C for 20 h. Analogously to our observations, unreacted double bonds were not detected in their work at a long enough reaction time.

Using our diadduct (formed at 20°C) as the initiator to polymerize styrene, a polystyrene was obtained with a monodispersed molecular weight distribution and a molecular weight expected from a diinitiator (as shown in the middle column of Table 1). Since this monodispersed MWD and expected molecular weight did not discriminate a one-end initiating process from a two-end initiating process, other methods had to be sought to prove whether the diadduct was indeed a diinitiator. Unlike previous researchers, who added *n*-BuLi in excess over DIPB to produce a mixture of the 1,3-bis(1-lithio-1-methylhexyl)benzene diadduct and the residual mono-initiating *n*-BuLi, we purposely prepared, by reacting stoichiometric *n*-BuLi with DIPB at 0°C, an initiator



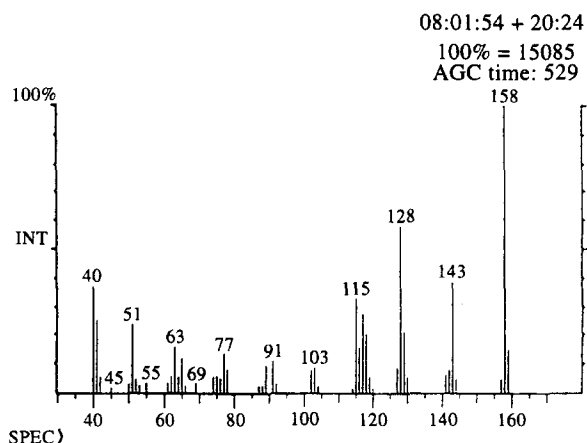
M.W. = 158



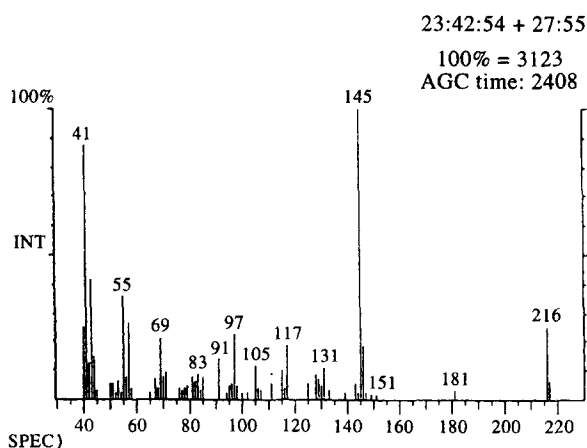
M.W. = 216

Scheme 5

mixture containing not only 1,3-bis(1-lithio-1-methylhexyl)benzene diadduct and *n*-BuLi but also 1-(1-lithio-1-methylhexyl)(3-isopropenyl)benzene monoadduct (shown in *Scheme 4*). The incomplete reaction at this



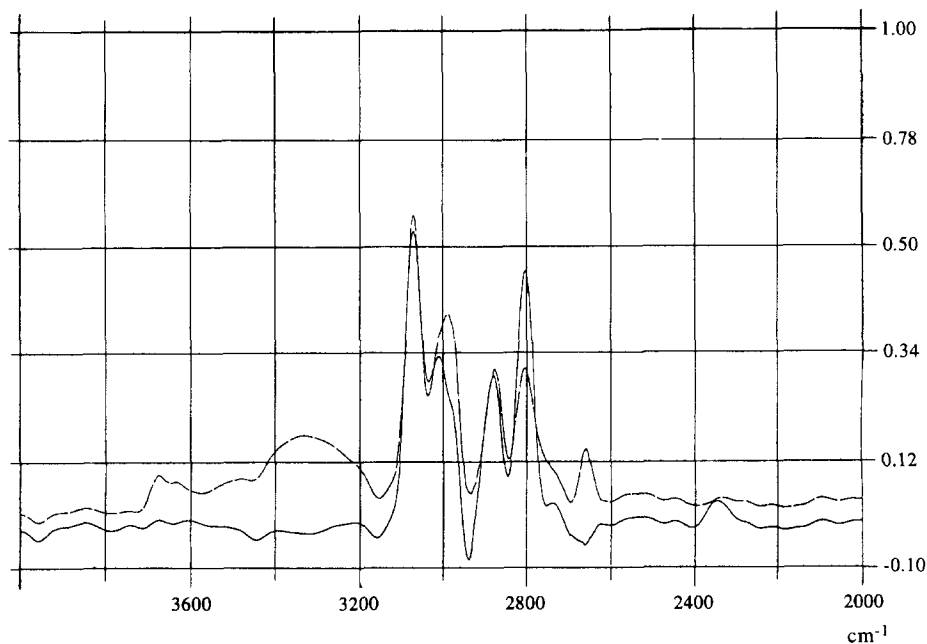
**Figure 5** M.s. spectrum of the g.c. peak 3 at 20:24



**Figure 6** M.s. spectrum of the g.c. peak 2 at 27:55

low temperature was corroborated by FTi.r. analysis of the remaining double bonds of DIPB (as illustrated in *Figure 1*) and the g.c./m.s. analyses of the various species after hydrolysis. Peaks #3 and #2, in addition to peak #1 representing the derivative of the diadduct, in the g.c. chromatogram in *Figure 4* pertained to *m*-diisopropenylbenzene and the derivative of the monoadduct (*Scheme 5*), having parent ions of *m/e* 158 and 216, respectively, as corroborated by the m.s. spectrum in *Figures 5* and *6*. Using such a mixture of various initiators to polymerize styrene, the outcome should be a bimodal molecular weight distribution provided that the diadduct reacted as a difunctional initiator. (The possible presence of small amounts of multifunctional initiators did not affect the molecular weight distribution since they selectively formed difunctional living chains due to a rapid depolymerization of the oligomers upon monomer addition<sup>35</sup>. Nevertheless, a monomodal, narrow molecular weight distribution was observed. The molecular weight of the synthesized polystyrene was smaller than that obtained previously using the initiator system formed at 20°C. This smaller molecular weight corroborated the inactivity of one of the two carbon–lithium ends on the diadduct, and the fact that the diadduct behaves as a monofunctional initiator in apolar solvent is consistent with previous findings<sup>35,36</sup>. The comparison between our two initiator systems formed at two different temperatures is shown in *Table 1*.

The initiator system made at 20°C, containing the diadduct with one inactive end, was next used for the synthesis of HTPB. The synthesis was carried out at 40°C in the presence of varying amounts of THF ranging from 0.02 wt% to 2 wt% of total solution. Any further increase in the THF would cause a decrease in the content of 1,4-microstructure which was required to attain elastomeric properties. The terminal hydroxyl groups on the polybutadiene arose from the capping reaction of the living polybutadienyllithium with oxetane followed by methanol termination. Their existence was evidenced by the absorption band in the



**Figure 7** FTi.r. spectrum of HTPB before and after oxetane capping (bottom: before; top: after)

3200–3400  $\text{cm}^{-1}$  of the FTi.r. spectrum such as that shown in Figure 7. Quantitative analysis of the hydroxyls was done using  $^1\text{H}$  n.m.r.,  $^{13}\text{C}$  n.m.r. and a direct titration method. The results of direct titration agreed with that of  $^1\text{H}$  n.m.r., and either analysis method indicated that in all cases the number of hydroxyls exceeded half of the starting number of carbon–lithium ends and could even reach greater than 80% of the starting number of carbon–lithium ends. Furthermore, the capping efficiency, defined as the ratio of the number of hydroxyls to the starting number of carbon–lithium ends, increased with an increase in the amount of THF added during the polymerization, as is shown in Figure 8.

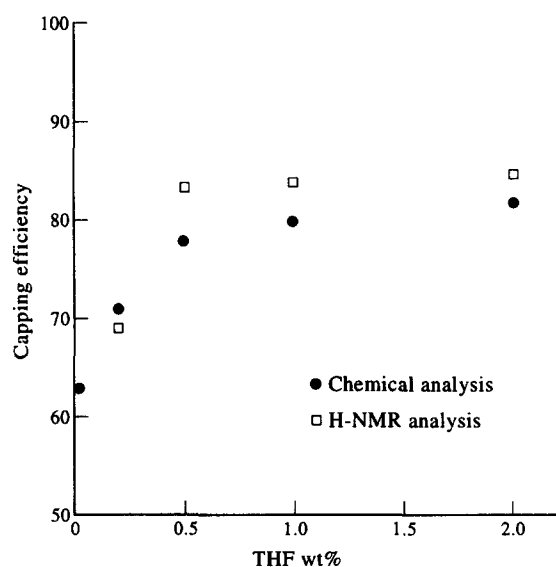


Figure 8 Efficiency of the capping reaction of carbon–lithium chain ends on  $\alpha,\omega$ -HTPB with oxetane at 40°C

However, the number derived from  $^{13}\text{C}$  n.m.r. differed from that derived from  $^1\text{H}$  n.m.r. by a factor of approximately 2.

Under 40°C and  $[\text{THF}] = 5000$  ppm experimental conditions, the  $^1\text{H}$  n.m.r. and  $^{13}\text{C}$  n.m.r. spectra obtained are shown in Figures 9 and 10, respectively. The  $\alpha$ -position carbon (i.e., the carbon atom  $\alpha$  to the hydroxyl group) was detected at 3.59 ppm in the  $^1\text{H}$  n.m.r. spectrum and at 63 ppm in the  $^{13}\text{C}$  n.m.r. spectrum. When normalized against the amount of 1,2-polybutadiene (i.e., a peak at 4.8–5.1 ppm in the  $^1\text{H}$  n.m.r. spectrum and at 114 ppm in the  $^{13}\text{C}$  n.m.r. spectrum), it was found that the amount of  $\alpha$ -position carbon differed by half, i.e. 0.347/11.828 from  $^1\text{H}$  n.m.r. vs 0.016/1.000 from  $^{13}\text{C}$  n.m.r. This was an unsurprising result since the hydroxyls stemming from the active end were neighbouring to a butadiene unit while those from the inactive end were neighbouring to isopropenylbenzene. Therefore, this different environment could cause a significant chemical shift in the  $^{13}\text{C}$  n.m.r. spectrum for the  $\alpha$ -position carbons on the inactive ends. This difference between  $^1\text{H}$  n.m.r. and  $^{13}\text{C}$  n.m.r. strongly suggested that whilst our diadduct functioned as a monoinitiator with one carbon–lithium end inactive as described previously, both carbon–lithium ends could be end-capped forming an  $\alpha,\omega$ -difunctional polybutadiene.

To fortify this conclusion and to prove the consistency between the two n.m.r. techniques, a  $^1\text{H}$  n.m.r. spectrum and a  $^{13}\text{C}$  n.m.r. spectrum were also taken on a monofunctional HTPB sample which was made using *n*-BuLi as the monoinitiator in the presence of 200 ppm THF in cyclohexane solvent, and compared against each other. While the microstructure of this HTPB was different due to the use of a smaller amount of THF, the amounts of  $\alpha$ -position carbons determined

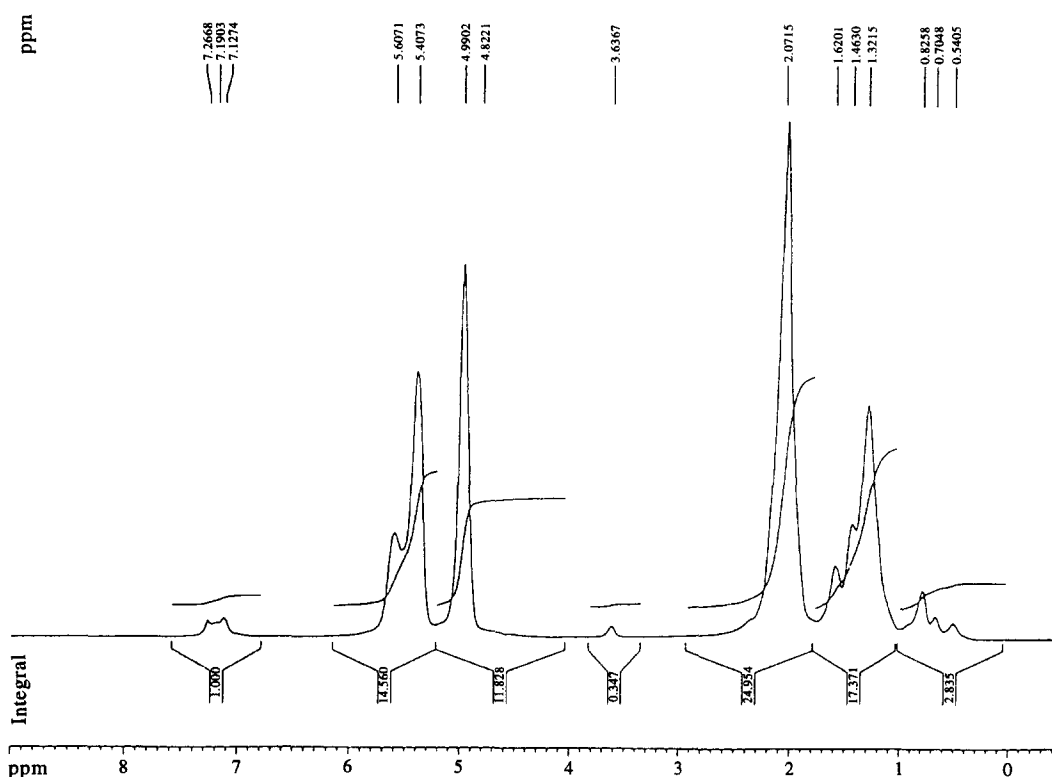


Figure 9  $^1\text{H}$  n.m.r. spectrum of  $\alpha,\omega$ -HTPB synthesized using diadduct at 40°C in the presence of 5000 ppm THF

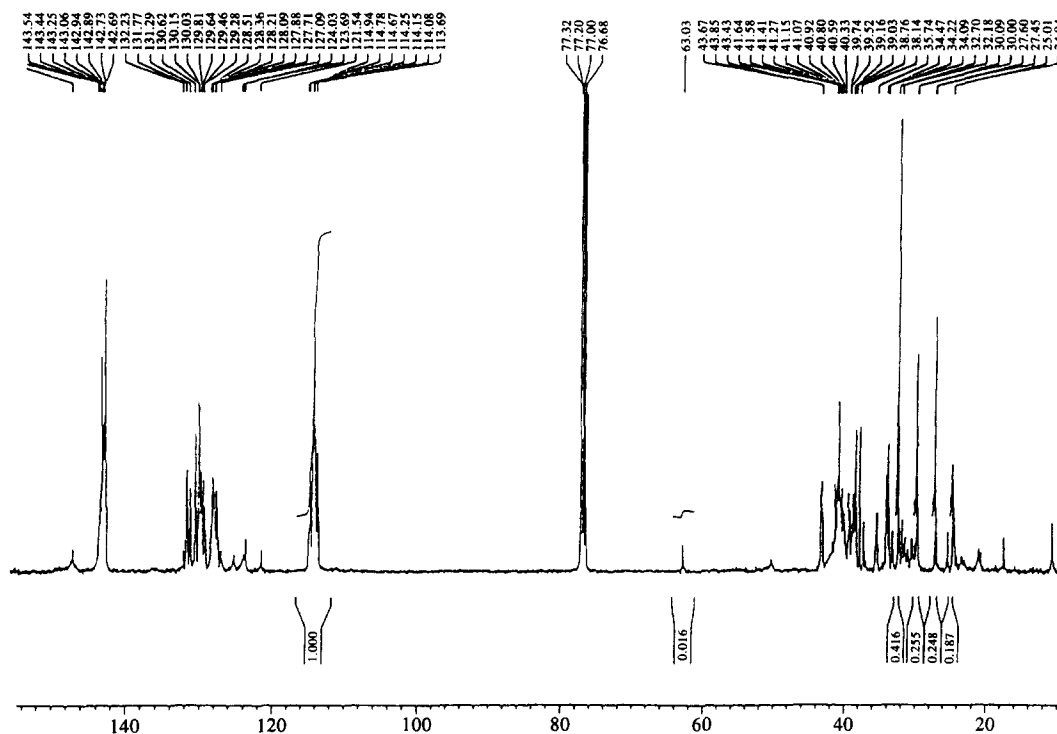


Figure 10  $^{13}\text{C}$  n.m.r. spectrum of  $\alpha,\omega$ -HTPB synthesized using diadduct at  $40^\circ\text{C}$  in the presence of 5000 ppm THF

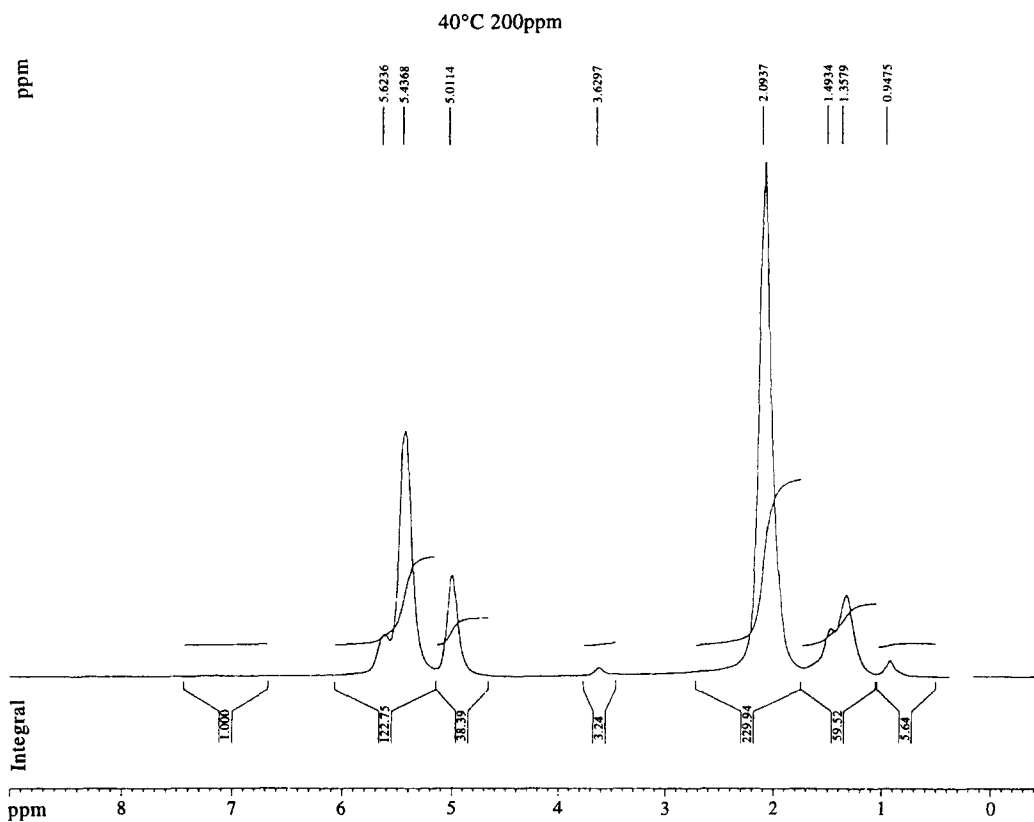


Figure 11  $^1\text{H}$  n.m.r. spectrum of monofunctional HTPB synthesized using *n*-BuLi at  $40^\circ\text{C}$  in the presence of 200 ppm THF

from these two spectra were, contrary to the  $\alpha,\omega$ -HTPB made using 1,3-bis(1-lithio-1-methylhexyl)benzene as the initiator, nearly the same as are shown in Figures 11 and 12, i.e. 3.24/38.39 from  $^1\text{H}$  n.m.r. vs 0.081/1.000 from  $^{13}\text{C}$  n.m.r. Therefore, upon capping the poly(butadienyl)-dilithium made using 1,3-bis(1-lithio-1,3-methylhexyl)-benzene as the initiator, if only the active lithium ends

had been able to be capped by oxetane, the  $^{13}\text{C}$  n.m.r. results and  $^1\text{H}$  n.m.r. results would have been in agreement. Thus, it was concluded that the lithium end which was inactive during the polymerization could undergo the capping reaction and thus be functionalized.

Furthermore, on the basis of this normalized hydroxyl content, the capping efficiencies have been calculated

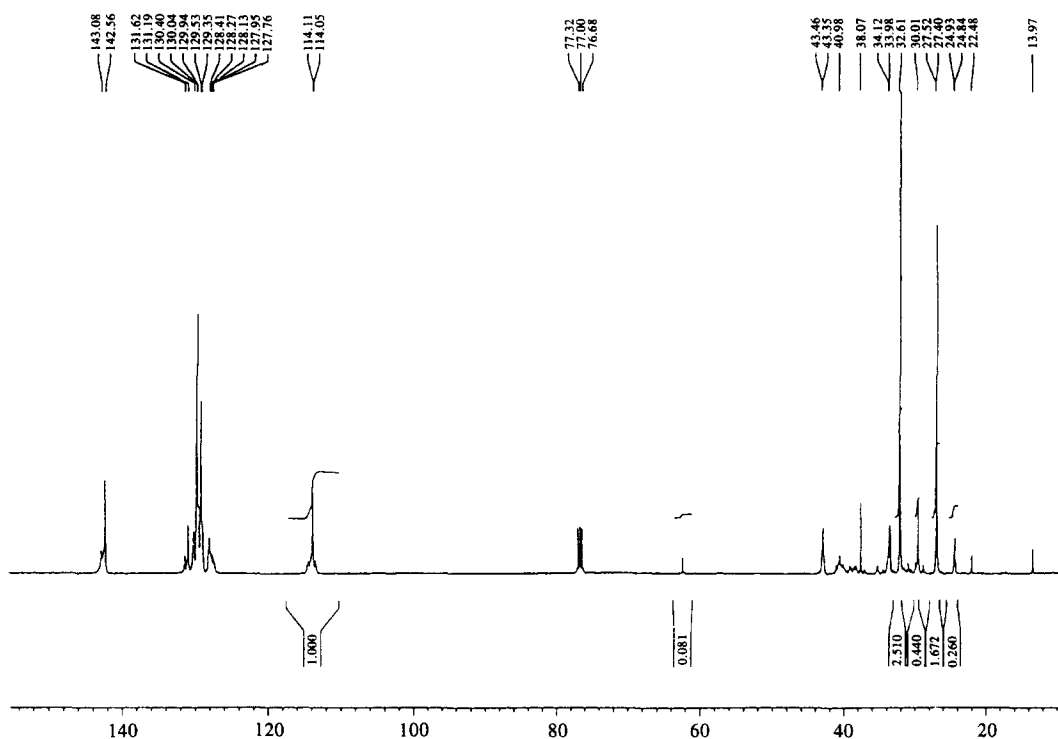
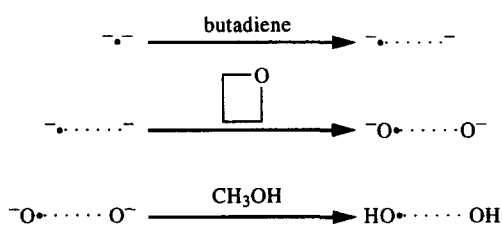


Figure 12  $^{13}\text{C}$  n.m.r. spectrum of monofunctional HTPB synthesized using *n*-BuLi at  $40^\circ\text{C}$  in the presence of 200 ppm THF

Table 2 Analytical data from  $^1\text{H}$  n.m.r. and  $^{13}\text{C}$  n.m.r. spectra

	Using diadduct		Using <i>n</i> -BuLi	
	$^1\text{H}$ n.m.r.	$^{13}\text{C}$ n.m.r.	$^1\text{H}$ n.m.r.	$^{13}\text{C}$ n.m.r.
1,2-PolyBD area	5.914	1.000	19.195	1.000
$\alpha$ -Carbon area	0.1735	0.0160	1.62	0.081
Mole ratio of 1,2-polyBD to hydroxyls	34.08	62.50	11.84	12.34
Capping efficiency	83%	45%	85%	82%



Scheme 6

and tabulated in Table 2. The polybutadiene made using 1,3-bis(1-lithio-1-methylhexyl)benzene diadduct was as efficient for reacting with oxetane as that made using *n*-BuLi (although more THF was needed for the former). The capping efficiency was 83% for the former and 85% for the latter (in accordance with  $^1\text{H}$  n.m.r. spectra), and the inactivity of one of the two carbon–lithium ends towards the polymerization did not prevent the 1,3-bis(1-lithio-1-methylhexyl)benzene diadduct from being an effective initiator for making telechelic HTPB. The overall  $\alpha,\omega$ -HTPB synthesis reaction proceeded as shown in Scheme 6.

## CONCLUSIONS

The diadduct made from 2 moles of *n*-butyllithium and 1 mole of *m*-diisopropenylbenzene has been evaluated as a diinitiator for synthesizing  $\alpha,\omega$ -hydroxyl terminated polybutadiene in cyclohexane solution. The g.c./m.s. analysis of the initiating species in conjunction with the observed monomodal molecular weight distribution clearly indicated that the formed diadduct did not react as a diinitiator but rather as a monoinitiator. Although one of the two carbon–lithium ends of the diadduct was inactive during the polymerization, both ends were able to react with oxetane, thus successfully forming the  $\alpha,\omega$ -hydroxyl terminated polybutadiene. This monofunctionality during polymerization and difunctionality towards the capping reaction has been corroborated by  $^1\text{H}$  n.m.r. and  $^{13}\text{C}$  n.m.r. spectra and titration results. The polybutadiene made using 1,3-bis(1-lithio-1-methylhexyl)benzene diadduct was as efficient for reacting with oxetane as that made using *n*-BuLi. The inactivity of one of the two carbon–lithium ends did not prevent 1,3-bis(1-lithio-1-methylhexyl)benzene diadduct from being an effective initiator for making telechelic HTPB.



## ACKNOWLEDGEMENTS

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