An efficient bifunctional lithium–organic initiator to be used in apolar solvents

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Upon reaction of *m*-diisopropenylbenzene (DIB) with two mole equivalents of s-butyllithium (BuLi) in benzene solution a diadduct is formed predominantly. It was identified by proton n.m.r. and by mass spectrometry. Some oligomers are formed, next to the diadduct, at the expense of the monoadduct. When the addition reaction is carried out to completion, precipitation eventually occurs. If this solution is used as it is formed, before precipitation has occurred, to initiate the polymerization of styrene or of dienes in non-polar solvents, the polymers formed exhibit the molecular weights expected, narrow molecular weight distributions and two lithium-organic sites per polymer chain. This bifunctional lithium-organic initiator is efficient, in the absence of any polar additive, and should find suitable applications for the synthesis of triblock copolymers, of model networks and of telechelic polymers.

Keywords Anionic polymerization; bifunctional initiator; nonpolar solvents; lithium; organic; polydienes

INTRODUCTION

A great deal of effort has been devoted in recent years to develop efficient bifunctional lithium–organic initiators that could be used in non-polar solvents. Such initiators are of special interest for diene polymerization when high 1,4 unit contents are wanted. Polymers bearing lithium–organic sites at both ends of their chain are currently used for the synthesis of telechelic polymers, of triblock copolymers and of model networks.

The various pathways that have been attempted to obtain bifunctional lithium–organic initiators have been reviewed recently[1–3]. We have focused our attention on the diadduct arising from the reaction of butyllithium with *m*-diisopropenylbenzene in non-polar media. Above 30°C, *m*-diisopropenylbenzene (DIB) does not polymerize; more precisely, its equilibrium concentration at that temperature is far above the concentration used in our experiments. Furthermore the double bonds of *m*-DIB are not conjugated and they behave quite independently.

This reaction has been studied by several authors[4–9]. It was concluded that the reaction product was a precipitate which was unable to initiate efficiently the polymerization of dienes, unless polar additives, such as amines or anisole, had been added. We have thoroughly studied this supposedly poor initiator and we come to dramatically different conclusions. The publication[3] in which our early results were disclosed encountered sharp criticism[4,5] concerning the synthesis of that bifunctional initiator in the absence of polar additive, as well as its ability to initiate the polymerizations of monomers such as styrene or dienes. The use of polar additives has been generally advocated, to fulfil these conditions. All the present work was carried out in the absence of polar additive.

The only other work performed under similar conditions was published recently by Sigwalt, Fontanille *et al.*[2,10] Here efficient bifunctional lithium–organic initiators were obtained by reacting butyllithium with either bis(*p*-isopropenylphenyl)alkanes, or 2,$(n-1)$-diphenylalkadienes, in non-polar solvents and in the absence of polar additives. These authors took advantage of the reversibility of the polymerization of α-methylstyrene type monomers[11], and their results concur with ours in many respects. The only drawback of Sigwalt's procedure is the rather difficult synthesis of the starting materials. DIB is much easier to synthesize.

This paper is concerned with the characterization of the lithium–organic compounds formed upon reaction of BuLi with DIB. The efficiency of this solution as a bifunctional initiator is examined.

EXPERIMENTAL

Solvents

Benzene and cyclohexane were distilled over sodium wire, and once more after addition of some BuLi, to make it water-free.

Monomers

Styrene and isoprene were purified and dried according to classical procedures (distillation over BuLi). *m*-Diisopropenylbenzene was synthesized and purified as described earlier[12].

'Diadduct' formation

The reaction between butyllithium and *m*-DIB was carried out in a stirred reactor, under argon atmosphere, in benzene solution, at temperatures ranging between 35° and 52°C, the duration of the reaction ranged from 30 min to 2 h.

Polymerization experiments

In most cases a calculated amount of monomer was slowly added to the 'diadduct' solution of known concentration, at 20°–30°C, under inert atmosphere. Thereafter the reaction mixture was kept at 45°–50°C for

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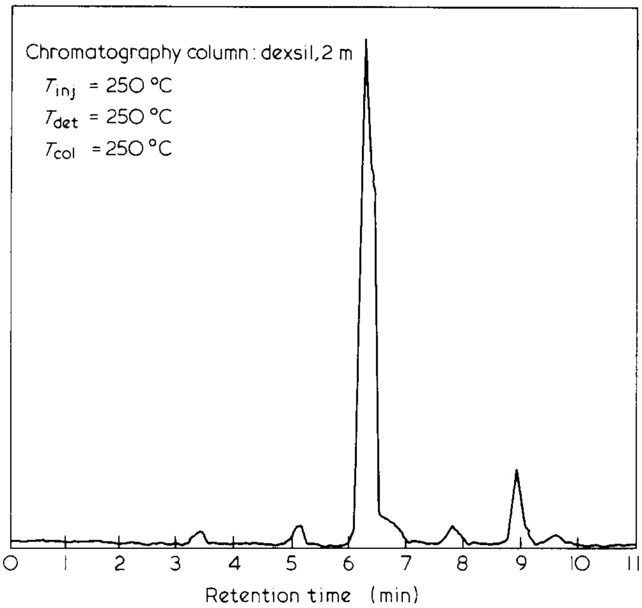


Figure 1 Vapour phase chromatography of the product: *m*-DIB/2 BuLi

an hour (55–60°C for isoprene), to ensure quantitative conversion into polymer. Thereafter the 'living' sites were deactivated protonically (methanol). It can also be treated with oxirane, whereby the reaction mixture gels. A few drops of acetic acid will protonate the alcoholate end groups and destroy the association phenomena whereby the solution becomes fluid again.

Characterization

Two different g.p.c. instruments have been used. One is specially designed to characterize low oligomers adequately. It is fitted with refractometric and u.v. spectroscopic detection. This set-up was used to characterize the compounds formed in the 'diadduct' solution, and the very low molecular weight polymers as well.

The other g.p.c. apparatus is standard Waters equipment fitted with refractometric and viscosimetric detection. It was used for the characterization of all polymers.

A Fica light scattering instrument was used for the weight average molecular weight determinations, and for the radii of gyration as well.

Hydroxyl group determination was carried out by phosgenation, followed by evaporation, and back-titration of the chloroformates formed.

SYNTHESIS AND CHARACTERIZATION OF THE DIADDUCT BETWEEN S-BUTYLLITHIUM AND *M*-DIISOPROPENYLBENZENE

When *m*-diisopropenylbenzene (DIB) is reacted at 40°C (or above), in dilute benzene solution, with two mole equivalents of s-butyllithium, the reaction medium slowly turns red, and it can be used after an hour (or more) to initiate the polymerization of styrene, butadiene, or isoprene. If instead the mixture is reacted for longer times at 40°C a precipitate is formed, thus showing that bifunctional lithium–organic compounds are in fact insoluble in apolar solvents. This was also experienced by Sigwalt[2,10].

Kinetics of adduct formation

To investigate the rate of addition of BuLi onto the double bonds of DIB a large excess of BuLi was reacted with the DIB, and the adduct formation was followed spectrometrically[12]. The main advantage of the large excess of BuLi was to prevent precipitation of the diadduct, once it is formed. Moreover it facilitates the kinetic treatment, as the BuLi concentration can be considered to stay constant. It was established that *m*-DIB is about twice as reactive as α-methylstyrene, which means that each double bond of DIB has the same reactivity as the α-methylstyrene double bond. Both steps of the addition proceed with the same rate constant, contrary to what is observed with *p*-DIB. The difference between these isomers, as far as reactivity is concerned, is due to the conjugation of double bonds in the *p*-DIB. It should be mentioned also that the adduct formation is much slower when cyclohexane is used instead of benzene.

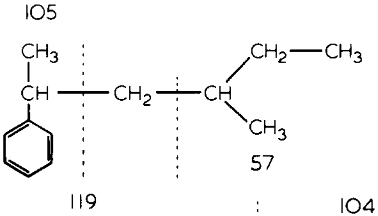
Characterization of the diadduct

To characterize the reaction product we reacted excess BuLi with *m*-DIB at 50°C in benzene solution for 4 h. After protonic deactivation of the carbanionic sites, filtration and evaporation of the solvent, the crude product was submitted to vapour phase chromatography and the major peak (*Figure 1*) was identified by mass spectrometry as the diadduct expected. The results are shown in *Table 1*, together with data on the mass

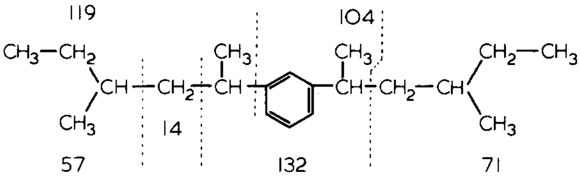
Table 1 Mass spectrometry of the diadduct of BuLi onto DIB, and of the BuLi adduct onto α-methylstyrene, after protonation of the carbanionic sites[a]

m/e	α-MS/BuLi adduct (%)	DIB/BuLi diadduct (%)	Observations
276		9	parent peak ($\underline{\alpha}$)
203		80	= 132 + 71
176	8		parent peak ($\underline{\beta}$)
133		100	= 132 + 1 proton
119	2		
105	100	75	= 104 + 1 proton
91	52	26	tropylium
77	48	5	phenyl
71		3	2-methylpentyl
57	6	97	s-butyl

Assignments



α-methylstyrene/BuLi adduct ($\underline{\beta}$)



DIB/BuLi diadduct ($\underline{\alpha}$)

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[a] Reaction conditions: solvent, benzene; 3-fold excess of BuLi; temperature, 50°C; reaction time, 4 h, thereafter deactivation with methanol

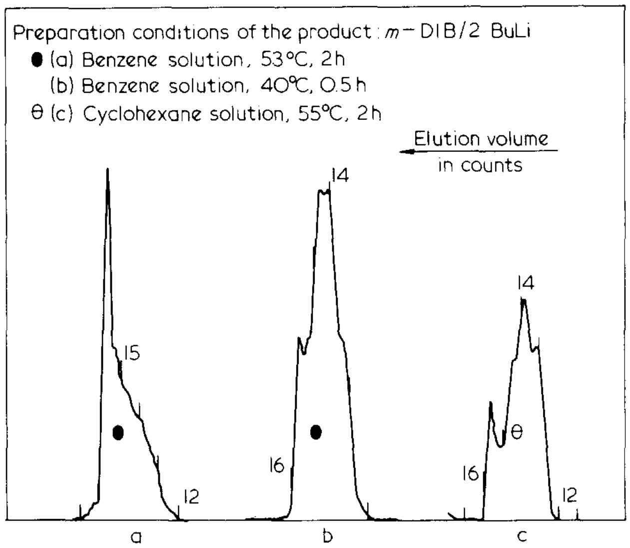


Figure 2 G.p.c. diagrams of DIB/2 BuLi prepared under various experimental conditions

spectrogram of the BuLi adduct on α-methylstyrene, taken for comparison.

Influence of reaction conditions on the adduct yield

The question arises as to whether the diadduct is also the major product formed under the experimental conditions generally chosen for the actual initiator synthesis: no excess butyllithium, dilute solution, temperature 40–50°C, reaction times 30–60 min (2–3 h when cyclohexane is the solvent). The various samples were deactivated protonically, and characterized by means of a gel permeation chromatograph specially equipped for low molecular weight samples. Refractometric and u.v. spectroscopic detections were used. Calibration was carried out by means of styrene oligomers so that only relative comparisons are possible. Typical chromatograms are shown in *Figure 2*. It can be seen that all reaction mixtures investigated contain oligomers next to the diadduct. The proportion of diadduct increases slowly with reaction time. The amount of monoadduct present is always low, which indicates that the oligomers are formed mainly at the expense of the monoadduct; in turn they react slowly with BuLi to form the diadduct. When excess butyllithium is present the proportion of oligomers formed is much lower.

In the case of the butyllithium adduct onto α-methylstyrene, the chromatographic peak is split, owing to stereoisomerism, as checked by mass spectrometry. The width of the peak corresponding to the BuLi/DIB diadduct probably also originates from stereoisomerism. The actual separation of stereoisomers is apparently impossible by the chromatographic technique that we used.

It is thus established that oligomers are present in the 'diadduct' solutions that we currently used as bifunctional polymerization initiators. An extension of the reaction time—aiming at an increase of the diadduct yield—does not help, as precipitation occurs as soon as 85% of all double bonds have undergone addition. The associations between lithium–organic sites in non-polar solvents are responsible for the precipitation which has even been observed sometimes in the presence of polar additives. In the recent work of Sigwalt *et al.* already quoted[2,10], the diadduct also precipitates in spite of the larger distance between lithium–organic sites, and of the higher flexibility of the base molecules chosen. Only a large excess of butyllithium can prevent precipitation: this is due to competitive association of the diadduct with remaining butyllithium.

Summarizing, it can be stated that the addition reaction of BuLi onto *m*-diisopropenylbenzene, in benzene solution, under conditions chosen such as to prevent DIB polymerization, is slow and rather complicated. In its early stages DIB is consumed to yield adducts and oligomers; gradually the diadduct yield increases at the expense of the oligomers; however precipitation then occurs, as a result of multiple associations between lithium–organic sites.

EFFICIENCY OF THE BUTYLLITHIUM–DIISOPROPENYLBENZENE 'DIADDUCT' AS POLYMERIZATION INITIATOR

In our previous paper[3] we have already shown that polymers obtained using the DIB/BuLi solution—which we shall call 'diadduct' for short, though keeping in mind its complexity—as initiator exhibit molecular weights close to the values expected, and sharp molecular weight distributions. Evidence for the bifunctional character of these polymers has also been presented. We shall now discuss the efficiency of that system as a bifunctional initiator, in non-polar solvents, on the basis of new results. We shall also critically examine the effect of the conditions of adduct formation on the initiator efficiency, and on the nature of the polymers formed. Finally we shall consider the stereoregularity of polyisoprenes obtained by means of this bifunctional initiator.

Molecular weights and polydispersity of polymers initiated by the 'diadduct' solution

If the 'diadduct' solution behaves as an efficient bifunctional lithium–organic initiator for the polymerization of the monomers investigated (styrene and dienes), the polymers should exhibit molecular weights that are twice those calculated from the mole ratio [monomer]/[BuLi] introduced. However we know that some monofunctional initiator is still present (chiefly unreacted BuLi) at the time the monomer is added. Calculation revealed that monofunctional species, if present to less than 10%, are not detectable owing to the limits of accuracy of the measurements: their effect on the molecular weight of the sample and the resulting broadening of the molecular weight distribution are too small.

On the other hand, if the plurifunctional oligomers also contributed to initiation, star-type macromolecules would result. Such species would mainly enhance the weight average molecular weight, obtained by light scattering. Moreover the star-shaped polymers would carry a lithium–organic site at the end of each branch.

The characterization data of a series of polymers initiated by the 'diadduct' solution are gathered in *Table 2*. In all cases quoted the adduct was formed under standard conditions ([BuLi]/[DIB] = 2). The monomer was added to the 'diadduct' solution prior to the precipitation of the active species, i.e. at a time at which at least 10–15% of the double bonds had not undergone reaction with BuLi, and at which oligomers are still present in the initiator solution (and unreacted BuLi, as well).

Table 2 Characterization data of polymers initiated with the BuLi/DIB 'diadduct' solution[a]

Ref. no.	Monomer	M_{th}	M_n (g.p.c.)	M_w (g.p.c.)	M_w (LS)
2190	Styrene	3 300	3 200	3 500	–
2176	Styrene	12 000	10 700	12 200	12 100
2263	Styrene	13 500	11 800	13 200	–
2424	Styrene	49 000	49 900	60 000	60 000
2423	Styrene	100 000	86 000	116 000	108 000
2203	isoprene	4 400	5 700[b]	6 300[b]	–
2458	isoprene	9 000	12 200[b]	13 600[b]	9 500
2453	isoprene	16 000	21 900[b]	27 000[b]	19 500
	isoprene	30 000	33 800[b]	41 000[b]	31 500

[a] Preparation of diadduct solution, [BuLi]/[DIB] = 2; solvent, benzene; temperature, 40°C; reaction time, 0.5–1 h

[b] Values obtained with PS calibration of g.p.c. M_{th}, molecular weight calculated from the ratio [monomer]/[DIB]; LS, light scattering

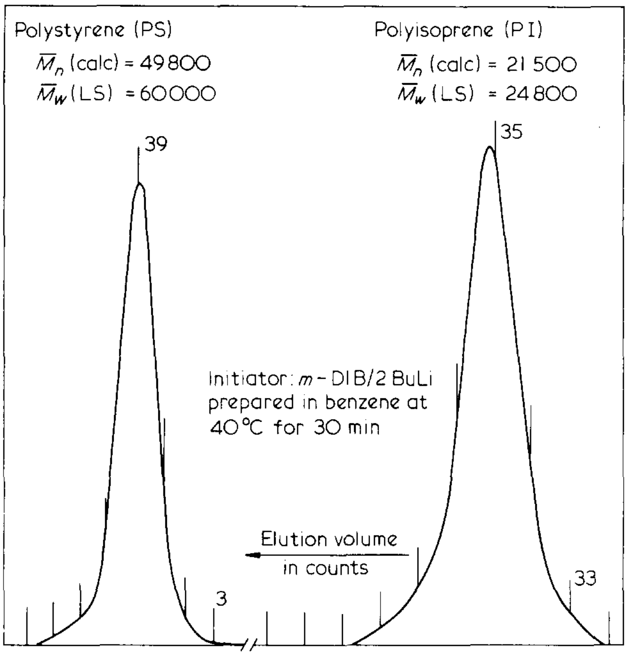


Figure 3 G.p.c. diagrams of polymers prepared with DIB/2 BuLi

Table 3 Characterization of the functionality of the polymers obtained with the 'diadduct' solution

Ref. no.	Deactivation	M_n (th)	M_n (g.p.c.)	M_n (OH)	M_w (g.p.c.)
2272	protonic	5 700	6 000	–	6 700
	oxirane	5 800	6 040	6 140	6 800
2278	protonic	4 200	5 700	–	6 400
	oxirane	4 300	5 500	4 100	6 100
2279	protonic	3 000	4 200	–	4 700
	oxirane	3 100	4 300	2 990	4 700
2280	protonic	10 100	10 000	–	11 300
	oxirane	10 200	10 500	10 000	11 700

Monomer: styrene

M_n (th), molecular weight calculated from the ratio [monomer]/[DIB]

M_n (OH), molecular weight determined from the OH content under the assumption of bifunctionality

Table 4 Polycondensation experiments with dibromo-*p*-xylene

M precursor	M polycondensate	Radius of gyration, $\langle r_g^2\rangle^{1/2}$ (Å) Exp.	Calc.	*P*
8 100	4 500 000	1456	1587	0.982
13 200	210 000	227	226	0.937

p = degree of conversion under the assumption of exact stoichiometry

$\langle r_g^2\rangle^{1/2}$ calculated, see text

The results displayed in *Table 2* call for a few comments:

In most cases the M_n values determined and expected differ by less than 10%.

The molecular weight distributions are generally quite narrow and unimodal. Two examples of g.p.c. elution curves are given in *Figure 3*.

Light scattering and g.p.c. yield very similar values of the weight average molecular weights.

The discrepancies observed with polyisoprenes are merely due to the fact that polystyrene calibration of g.p.c. was used.

Functionality of polymers initiated by the 'diadduct' solution

If the 'living' polymer obtained upon initiation with the 'diadduct' solution is deactivated with oxirane, a physical gel results—if the concentration is above c^*—owing to strong associations between alcoholate end groups. Upon protonation the gel is destroyed, and the macromolecules are fitted at both chain ends with alcohol functions: the M_n values resulting from functional analysis and from g.p.c. are in good agreement (*Table 3*).

Chain extension experiments were also carried out. A polymer obtained using the 'diadduct' solution as initiator is reacted with a stoichiometric amount of 1,4-bis(bromomethyl)benzene(dibromo-*p*-xylene). This compound does not give side reactions (elimination, or metal halogen interchange)[13] under the conditions chosen. The results are shown in *Table 4*: a very large increase of the molecular weight is observed. No gel is formed upon reaction, which indicates that species with more than 2 active sites per molecule can be neglected.

To test the linearity of the 'polycondensates', their radii of gyration were measured and compared with values calculated using the expression[14]:

$$\langle r_g^2\rangle^{1/2} = 9.45 \times 10^{-2}\ M^{0.635}$$

valid for polystyrene in THF solution. In spite of the fact that the radius of gyration is a *z*-average, and molecular weights determined by light scattering are weight ave-

Table 5 Polymers obtained using initiating solutions with a ratio [BuLi]/[DIB] = 3

Ref. no.	M_n^a (calc.)	M_w^a (calc.)	M_n (g.p.c.)	M_w (g.p.c.)	M_w/M_n
2382	5 100	5 700	6 400	7 100	1.11
2386	4 050	4 500	5 100	5 600	1.10
2405	11 200	12 500	12 700	14 800	1.17

Monomer: styrene

[a] M_n and M_w calculated under the assumption of equal amounts mono- and difunctional polymers, with molecular weights in the ratio 1:2

rages, the comparison is still significant, because of the low polydispersity of our samples.

From these results it follows that polymers initiated with the 'diadduct' solution are bifunctional to more than 90%, and that macromolecules with more than two lithium-organic sites are not detectable. These polymers exhibit molecular weights and polydispersities very close to those expected under the assumption of purely bifunctional initiation.

Polymers initiated with non-stoichiometric BuLi/DIB adduct solutions

We have carried out a few experiments with initiating solutions arising from non-stoichiometric mixtures of BuLi and DIB ([BuLi]/[DIB] $\neq 2$). When excess BuLi is present one can expect the initiating solution to behave as a mixture of bifunctional and monofunctional species. *Table 5* displays some results that were obtained with the system 3BuLi/DIB, after almost quantitative consumption of the double bonds. The solution should contain one remaining monofunctional initiator (BuLi) for each bifunctional 'adduct' formed. The molecular weights M_w and M_n calculated accordingly are only slightly lower than the values found, and the polydispersity indices are in the range expected.

When less butyllithium is present than needed for 'diadduct' formation, the occurrence of monoadduct and of oligomers should be privileged. Polymers obtained with such an initiating system should exhibit a branched structure and a molecular weight much higher than the values calculated assuming monofunctional initiation. This is what was observed (*Table 6*). The M_w values determined by light scattering are somewhat higher than the M_w values resulting from g.p.c., showing that the macromolecules formed are branched. It is thus confirmed that the monoadduct reacts preferentially with DIB to give oligomers that are potentially plurifunctional.

Influence of the reaction time on the initiating species formed in the 'diadduct' solution

To carry out this investigation, we reacted stoichiometric amounts of BuLi and DIB (mole ratio 2:1) in benzene solution, and we took samples at various reaction times. The amount of BuLi addition was estimated from the optical density of the 'living' solution, at these times. Each of the solutions sampled was then used to initiate the polymerization of a known amount of styrene, and the molecular weights of the polymer were compared with the values calculated under the assumption of bifunctional initiation. The results are shown in *Table 7*. The agreement between the M_w values originating from light scattering and from g.p.c. is good, which indicates that the polymers are essentially linear.

It can be stated that as soon as the degree of metallation of DIB reaches about 70% the reaction product between DIB and BuLi behaves as a bifunctional initiator. However these experiments lack accuracy; amounts of monofunctional species up to 10% cannot be detected.

Initiating efficiency of the 'diadduct' solution

We have shown above that the 'diadduct' solution still contains oligomers when it is used as a bifunctional initiator. We wanted to establish whether or not these species contribute to the initiation upon addition of styrene or isoprene to the 'diadduct' solution. For that purpose small amounts of monomer (5 to 20 molecules) were added to the 'diadduct' solution, and the g.p.c. diagrams taken before and after monomer addition were compared (*Figures 4* and *5*).

The molecular weight distribution of the polymers formed are very narrow, and the oligomers—present before monomer addition—have vanished entirely. The agreement between the values of M_n measured and calculated is satisfactory (*Table 8*). The data obtained with isoprene are most interesting, because of slow initiation. As more isoprene is added the molecular weight sharpens. Another point should be made here: the polyisoprene obtained exhibits the characteristic u.v. absorption of phenyl rings at 242 nm, which proves that initiation occurs by addition onto the monomer.

It is most likely that oligomers present in the 'diadduct' solution do not participate in the initiation. Moreover they depolymerize and very rapidly yield diadduct. This accounts for the good agreement between molecular weights measured and the values calculated under the assumption of quantitative diadduct formation.

Table 6 Polymers obtained using initiating solutions with a ratio [BuLi]/[DIB] = 1

Ref. no.	M_n^a (calc.)	M_n (g.p.c.)	M_w (g.p.c.)	M_w (LS)
2270	13 700	47 800	79 800	116 000
2373	10 200	40 300	45 800	49 000

Monomer: styrene

[a] M_n calculated under the assumption of monofunctional initiation:

$$M_n = m_0 \frac{[M]}{[BuLi]} = m_0 \frac{[M]}{[DIB]}$$

Table 7 Influence of reaction time of BuLi with DIB on polymers formed with the 'diadduct' solution

Ref. no.	Conversion of DIB double bonds (%)^a	M_n^b (calc.)	M_n (g.p.c.)	M_w (g.p.c.)	M_w (LS)
2376 A	50	15 700	10 900	13 000	12 600
B	70	17 200	14 100	16 400	16 800
C	90	16 900	16 900	19 400	20 100
D^c	–	15 500	15 000	17 300	18 700
2377 A	25	16 100	12 000	14 900	15 700
B	85	14 600	13 400	15 500	14 600
C^c	–	17 000	19 900	23 000	24 000

Monomer: styrene

[a] From the optical density at 315 nm, see ref. 10

[b] M_n calculated under the assumption of bifunctional initiation

[c] Diadduct had precipitated when monomer was added

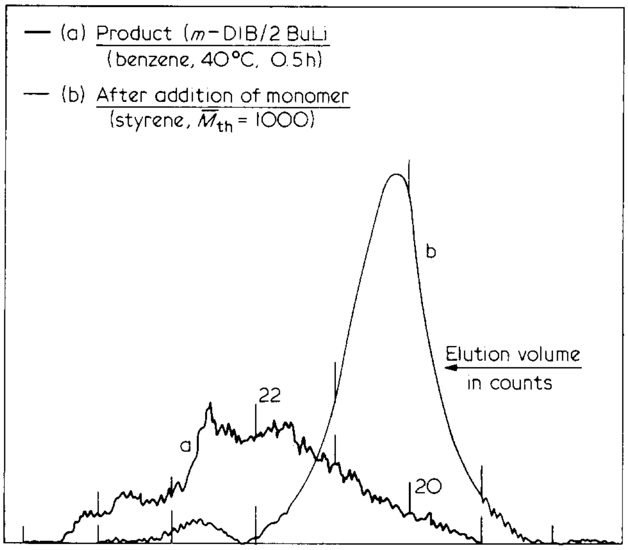


Figure 4 Characterization by g.p.c. of the initiation with DIB/2 BuLi, PS

When the reaction between BuLi and DIB is carried out under conditions chosen such as to enhance diadduct formation (elevated temperature and long reaction time) the initiating medium becomes heterogeneous, as already mentioned. Polymers initiated under these conditions exhibit broader molecular weight distributions, and also molecular weights slightly higher than expected. This is due to heterogeneous initiation, the diadduct being insoluble.

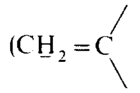
Stereoregularity of polyisoprenes obtained with the 'diadduct' solution as initiator

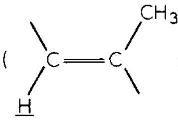
The microstructure of polyisoprenes obtained with the diadduct solution as initiator, in apolar solvents (benzene or cyclohexane), was investigated using two classical techniques: infra-red spectroscopy and proton n.m.r.

I.r. spectroscopy is well fitted to detect 1,2 or 3,4 units since the absorption coefficients are more than 10 times larger than those originating from the 1,4 *cis* or 1,4 *trans* units, as shown recently by Simak and Fahrbach[15]. The samples investigated did not exhibit any absorption at 907 cm^{-1} (1,2 units); only a weak peak was detected at 886.9 cm^{-1} (3,4 units).

More detailed results were obtained from n.m.r. spectra, using Tanaka's[16] calibration procedure.

The calculation based on the absorption peaks located

at 4.81 ppm ( $\mathrm{C\underline{H}_2{=}C\lessdot}$ 3,4),

at 5.24 ppm ( $\mathrm{\underline{H}C{=}C(CH_3)}$ *trans* 1, 4)

and 1.65, 1.69 and 1.74 ppm (methyl protons, respectively, of 3,4 *trans* 1,4 and *cis* 1,4 units)

yielded the following results, quite reproducibly:

cis 1,4: 64%   *trans* 1,4: 27%   3,4: 9%

These values are in good agreement with those generally accepted for polyisoprenes obtained with BuLi in apolar solvents.

CONCLUSION

The most important result of this detailed investigation is that the adduct formation between butyllithium and *m*-diisopropenylbenzene does not require polar additives to be active as has been claimed many times. The 'diadduct' solution—which also contains some oligomers, next to the diadduct—acts as an efficient bifunctional lithium–

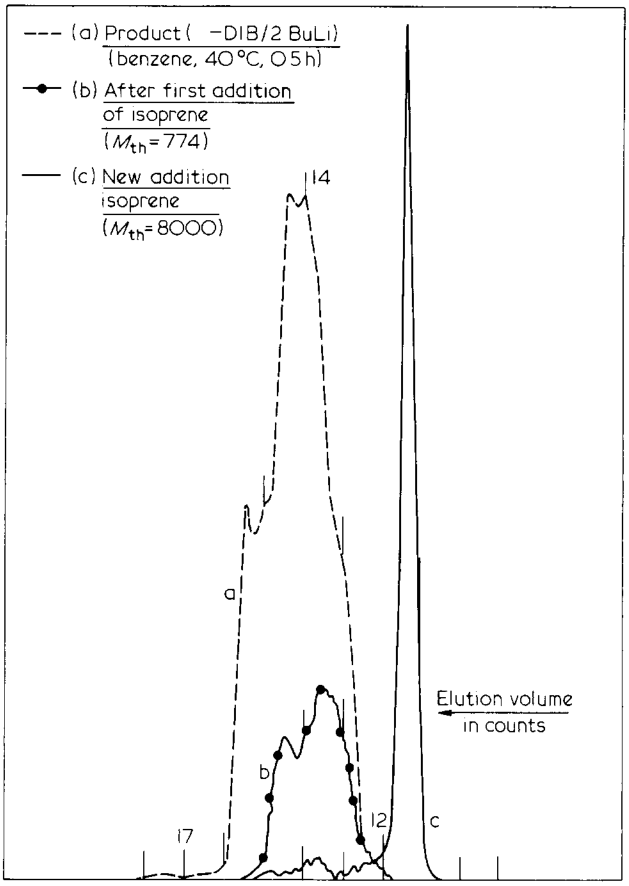


Figure 5 Characterization by g.p.c. of the initiation with DIB/2 BuLi, PI

Table 8 G.p.c. characterization of polyisoprene samples of lower molecular weights prepared with *m*-DIB/2 BuLi

Sample	$\bar{M}_n$ (th)	$\bar{M}$ (g.p.c.)[a]	
2518 (2)	774	1150	benzene $\bar{M}_w$ (g.p.c.) = 11 000
(3)	1274	2000	
(4)	2274	4000	
(5)	5034	10 000	
2531 (2)	774	350 and 650	(two peaks) benzene
(3)	1274	1200	
(4)	2274	1500	
(5)	8000	6500	
2516 (2)	774	800	cyclohexane
(3)	1274	1200	
(4)	2274	2000	

2518: initiator prepared in benzene solution for 4 h at 53°C, g.p.c. chromatogram shows mainly diadduct formation
2531: initiator prepared in benzene solution for 1/2 h at 40°C g.p.c. chromatogram shows diadduct but also oligomers
2516: initiator prepared in cyclohexane solution for 2 h at 53°C, g.p.c. chromatogram show diadduct but also oligomers
[a] Standard curve polyisoprene, molecular weight at the peak maximum

organic polymerization initiator for monomers such as styrene or diene, and here again no polar additive is necessary to enhance the initiation rate: the polymers exhibit the molecular weights expected, and sharp molecular weight distributions; they are essentially linear and carry lithium–organic sites at both chain ends. Taking into account the accuracy of the experimental characterization methods, one can state that more than 90% of the molecules formed are bifunctional, and that molecules exhibiting functionalities higher than 2 cannot be detected.

The 'diadduct' solution can be used as soon as 60% of the double bonds of DIB have undergone reaction with BuLi. At that time oligomers are present, but they do not contribute to the initiation process; the 'diadduct' solution behaves as if it contained only the diadduct. When the reaction between BuLi and DIB is carried out for longer times and/or at higher temperatures, the diadduct yield is greatly increased, but it soon becomes insoluble. Addition of monomer then results in heterogeneous initiation with the corresponding broadening of molecular weight distribution that arises from slow initiation.

It is difficult to account for the fact that upon monomer addition the oligomers present in the initiating solution vanish at once, and contribute quantitatively as diadducts to the initiation process. This is an experimental fact, explanations are yet speculative. Nevertheless the efficiency of the 'diadduct' solution as bifunctional initiator is clearly established, in purely apolar solvents: the microstructure of polyisoprenes obtained by this method is thus kept at the same level of 1,4 addition as it is with butyllithium as initiator.

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