Addition of sec-butyllithium to *m*-diisopropenylbenzene

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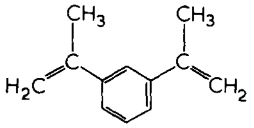
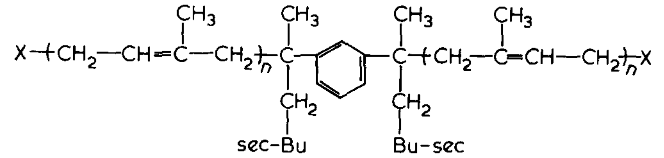
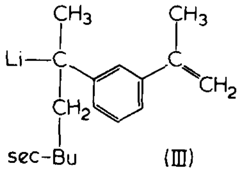
The reaction of equivalent quantities of sec-butyllithium with *m*-diisopropenylbenzene in cyclohexane and benzene solution in the presence and absence of catalytic amounts of triethylamine, does not yield the diadduct quantitatively. Oligomer formation occurs to varying extents depending on the reaction conditions, and, contrary to claims in the literature, this may not be a good route to a difunctional initiator for anionic polymerization.

Considerable effort has been devoted in recent years to the generation of a bifunctional anionic initiator that is soluble in non-polar solvents, the ultimate goal being the synthesis of telechelic polydienes with precisely controlled molecular weight, functionality and microstructure. Two groups have recently and independently claimed[1,2] a significant advance towards this goad by addition of sec-butyllithium to *m*-diisopropenylbenzene (I):


(I)

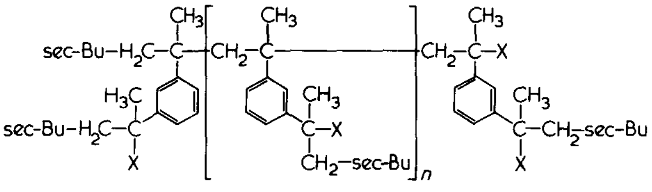

(II)
(a) n=0, X=Li
(b) n=5, X=Li
(c) n=0, X=H


(III)

Sharkey[1] and coworkers carried out the reaction in cyclohexane solution in the presence of triethylamine as catalyst and claimed the product to be (IIa), which they stabilized against agglomerization in the hydrocarbon solvent by building up short chains of polyisoprene to give (IIb). Rempp and coworkers[2], on the other hand, used benzene solution without a catalyst, and were of the opinion that initially only one molecule of butyllithium reacted with (I) giving (III), and that the second molecule reacted only after monomer was added to the system. Since this seems a rather unlikely sequence of events, we have examined more closely the effect of solvent and catalyst on the reaction of (I) with sec-butyllithium.

Two equivalents of sec-butyllithium were reacted with (I) at room temperature in benzene and in cyclohexane, both in the presence and absence of triethylamine at the recommended[1] concentration of 0.1 mol per mol of alkyllithium (*Table 1*, runs 1–4). The reactions were quenched with water, and effervescence was observed in every case, the effect being particularly marked in run 1. Rempp and coworkers noted[2] effervescence under similar circumstances, and ascribed it to the hydrolysis of unreacted butyllithium and cited this as evidence that (III) rather than (IIa) was the reaction product. However, in contrast to the findings of the French workers, we could not detect signals for residual unsaturation in the n.m.r. spectra of the isolated products. Even when equimolar amounts of (I) and sec-butyllithium were reacted (runs 5,6), the products showed no olefinic signals in the n.m.r. spectra, and still gave effervescence at the quenching stage. We conclude that unreacted (I) or any monoadduct (III) must constitute a very small proportion of the total product.

The most plausible explanation for these observations involves polymerization, or at least oligomerization, of the *m*-diisopropenylbenzene to give (IVa) or analogous branched structures:


(IV)
(a) X=Li
(b) X=H

Under this scheme, there is no unsaturation in the final product, and one molecule of sec-butyllithium is left unreacted per unit increase in the degree of polymerization.

The product from run 1 (wherein most effervescence was observed on quenching) was noticeably more viscous than the products from runs 2–4, while the products from runs 5 and 6 were highly viscous gums, and clearly were of high molecular weight.

Conclusive evidence for polymerization of (I) came from characterization of the products by gel permeation chromatography (g.p.c.). *Figures 1a–1f* show the traces obtained from products 1–6, several peaks corresponding to different molecular weights being present in each case, with products 1, 5 and 6 showing the greatest proportion of high molecular weight material.

For runs 2, 3 and 4, the major peak had the same elution volume (*EV*) in each case, corresponding to the component of lowest molecular weight, apart from one of two minor products with greater *EV*. Very little of this component was produced in run 1, but a peak corresponding to a com-

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Table 1 Summary of experiments performed

Run No.	Solvent	BuLi[a] Conc.	Et_3N[b] Conc.	Temperature	G.p.c. trace[c,d]
1	Cyclohexane	2.0	0	Room	*Figure 1a*
2	Cyclohexane	2.0	0.1	Room	*Figure 1b*
3	Benzene	2.0	0	Room	*Figure 1c*
4	Benzene	2.0	0.1	Room	*Figure 1d*
5	Cyclohexane	1.0	0.2	Room	*Figure 1e*
6	Benzene	1.0	0.2	Room	*Figure 1f*
7	Benzene	2.0	0	55°C	*Figure 1i*
8	Benzene	2.0	0.1	55°C	*Figure 1j*
9	Cyclohexane	2.0	0.5	Room	*Figure 1k*
10	Cyclohexane	2.0	1.0	Room	*Figure 1l*

[a] Moles per mole of (I)

[b] Moles per mole of BuLi

[c] Volume scale on Figures represents vol. of $CHCl_3$ passed from sample injection

[d] G.p.c. traces *1g* and *1h* from the distillate and residue respectively of combined products of runs 3 and 4

pound of slightly lower molecular weight is apparent in *Figure 1a*, together with peaks from the major, polymeric products.

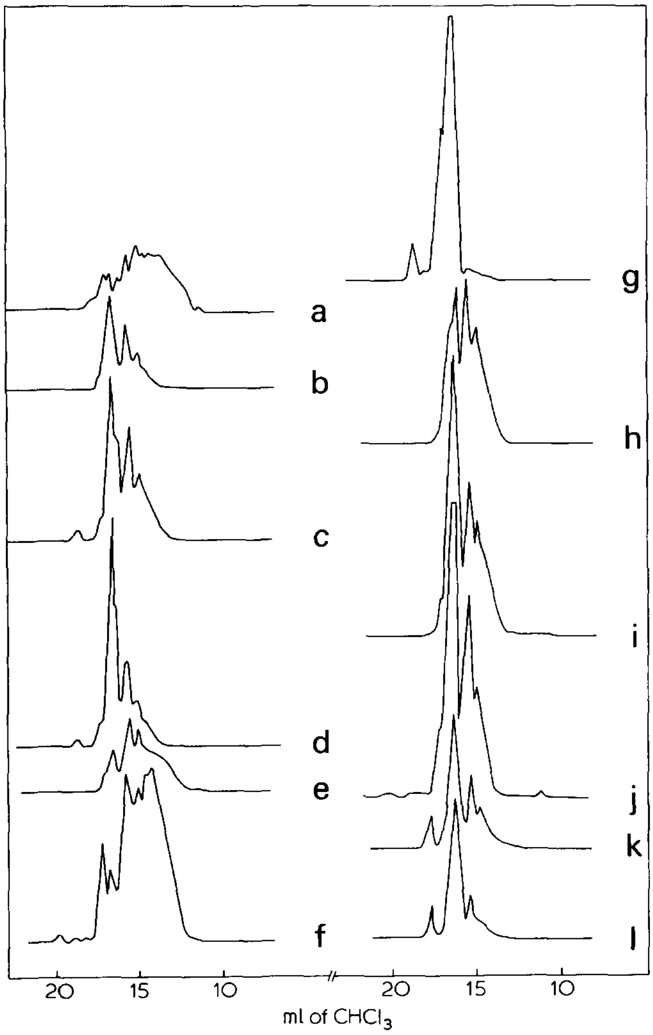
The combined products of runs 3 and 4 were distilled under reduced pressure to give a mobile oil as distillate and a viscous gum as residue. *Figures 1g* and *1h* show their respective g.p.c. traces. The latter shows the same set of peaks as in the original mixture, but with a drastic reduction in the proportion of low molecular weight material, while the former consists mainly of the major product in runs 2–4. The mass spectrum of the distillate gave m^+ as 274, consistent with (IIc). Hence it was concluded that (IIc) was the structure of the major poduct in runs 2–4, the higher molecular weight components having structure (IVb) ($n = 0, 1, 2$ etc.) or branched analogues thereof.

It therefore followed that the reaction of (I) with *sec*-butyllithium in cyclohexane solution in the absence of catalyst (run 1) produced hardly any of the desired bifunctional initiator, but gave mainly polymeric products with a small amount of different low molecular weight material. The identity of the latter has not been established, but it could be unreacted (I) and/or its monoadduct with butyllithium since Sharkey and coworkers found the reaction to be very sluggish in the absence of triethylamine. Significantly, this unknown compound all but disappeared from the product mixture (as evidenced by g.p.c.) on storage in a stoppered flask for several months, which suggested that the compound was capable of polymerization. There is also evidence of the presence of small amounts of compounds of lower molecular weight than (IIc) in other g.p.c. traces, particularly in *Figure 1f*, and this is consistent with the fact that run 6 was conducted with half of the quantity of butyllithium required to give (IIc) and hence polymer, monoadduct (III), and unreacted (I) are likely to be the favoured products.

The reaction in benzene solution was repeated at a higher temperature (approximately 55°C, bath temperature) (runs 7, 8) but g.p.c. indicated only a slight reduction in the proportion of oligomeric products (*Figures 1i* and *1j*). A comparison of *Figure 1c* with *Figure 1d* and *Figure 1i* (run 7) with *Figure 1j* (run 8) shows that the presence of triethylamine has comparatively little effect on the reaction of (I) with sec-butyllithium in benzene solution, but *Figures 1a* and *1b* show that the catalyst exerts a profound effect in cyclohexane solution. Runs 9 and 10 were conducted in the latter solvent at higher catalyst concentrations (0.5 and 1.0 molecules per lithio-site), and g.p.c. showed a progressive reduction in the concentration of polymeric product with increase in catalyst concentration (*Figures 1k, 1l*). However, the oligomers were not eliminated completely, and some effervescence was still observed at the quenching stage.

It appears that during the reaction of (I) with sec-butyllithium, a three-way competition exists between the lithio-sites in (IIa), (III) and the sec-butyllithium for reaction with the remaining vinyl groups, and that triethylamine promotes attack by the sec-butyllithium in preference to the other lithiated species, the effect being more pronounced in cyclohexane solution than in benzene. In the latter solvent, the addition of triethylamine speeded-up the reaction considerably (judged by the development of a deep red colour), but had comparatively little influence on the product distribution.

Working in hexane solution, Kamienski and Morrison[3] prepared separate solutions of (IIa) and (III) by treatment of (I) with the appropriate amount of sec-butyllithium in the presence of 1.0 mol triethylamine per mol of alkyllithium. By mixing the solutions, they then obtained the trifunctional initiator (IVa) ($n = 0$). This confirms that oligomerization is possible in this system, and illustrates the effect of increasing the triethylamine concentration. Our attempts to prepare (III) in cyclohexane in the presence of 0.2 mol catalyst per mol of sec-butyllithium gave mainly polymeric material (run 5, *Figure 1e*). (Although our results indicate that polymeric material is produced even at high catalyst concentra-



Figures 1a–1l G.p.c. traces of products of experiments summarized in *Table 1*

Table 2 Calculated integral ratios for ^{1}H n.m.r. spectra of (IIc) and (IVb)

Compound	Aromatic: Benzylic	Alkyl: Aromatic
(IIc)	2.0	7.5
(IVb) $n = 0$	2.7	6.3
(IVb) $n = 1$	3.1	5.8
(IVb) $n = 2$	3.2	5.6
(IVb) $n = 3$	3.3	5.5
(IVb) $n = 4$	3.4	5.4

tions, it is probably at a level sufficiently low to pass unnoticed under most circumstances).

Clearly, the formation of oligomeric material during the addition of sec-butyllithium to (I) has serious repercussions as far as the synthesis of bifunctional polymers is concerned. Instead of producing an exactly bifunctional initiator, the result is a mixture of bifunctional with mono- and polyfunctional material. Sharkey and coworkers claim that oligomerization takes place in the reaction between *m*-divinylbenzene and sec-butyllithium, but did not detect any in the corresponding reaction of *m*-diisopropenylbenzene. Likewise, Rempp and coworkers[2] are of the opinion that (I) reacts cleanly with sec-butyllithium without polymerization. It is therefore of interest to examine their results to see whether it is possible that they may unwittingly have encountered the oligomerization problem.

The American group[1] quenched samples of the adduct with water and with deuterium oxide, then recorded the n.m.r. spectra. No mention is made of effervescence at the quenching stage, but presumably this would be difficult to detect in small samples. No signals for benzylic protons were observed in the spectra of samples quenched with D_2O, while in the other samples the integral ratios for the aromatic and benzylic signals, and for the aliphatic and aromatic signals, were 2.0 and 7.5, respectively, consistent with structure (IIc).

The D_2O experiments provide no evidence either way on the question of polymerization, since neither structure (II) ($X = D$, $n = 0$) nor structure (IV) ($X = D$) should give a benzylic signal in the ^{1}H n.m.r. spectrum. The integral ratios mentioned above are also rather insensitive to the presence or absence of oligomeric material. *Table 2* lists the calculated values for structures (IIc) and (IVb), from which it is apparent that it might be difficult to distinguish pure (IIc) from its admixture with small amounts of oligomer. Certainly, in our own experiments, samples that were shown by g.p.c. to be mixtures gave integral ratios close to the theoretical values for structures (IIc), while the n.m.r. spectrum of the distillate from runs 3 and 4 was virtually identical to the spectrum of the original mixture.

Further characterization carried out by Sharkey and coworkers involved addition of isoprene to the initiator solution (5 molecules per lithio-site), carboxylation of the chain ends, conversion of the latter to the acid form, and titration of the acid groups with tetrabutylammonium hydroxide. From this they calculated the molecular weight per acid group, and found it to be consistent with a functionality of two. It could equally well be argued, however, that what they determined was the *average* molecular weight per acid group, and that it turned out to be consistent with an *average* functionality of two. In other words, a distribution of functionalities could have been present whose average was two, and this is exactly the situation that would develop if polymerization took place as a side reaction. As pointed out earlier, a unit increase in the degree of polymerization not only gives a molecule whose functionality has increased by one, but also leaves one molecule of monofunctional sec-butyllithium unreacted. Hence, if the unreacted butyllithium is taken into account, the average functionality is always exactly two. Thus, end-group titration is also ineffective in the detection of oligomeric material.

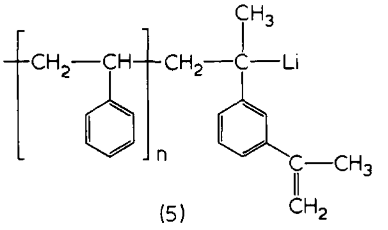
Perhaps the most difficult finding of Sharkey and coworkers to reconcile with the formation of a mixture of initiating species is the fact that they were able to produce low dispersity polymers of predictable $\bar{M}_n$. One normally associates a narrow, unimodal molecular weight distribution with a homogeneous initiator, but this does not appear to be the case in this instance. According to the American workers, increasing the triethylamine concentration from 0.1 to 1.0 molecules per lithio-site resulted in an increase in dispersity from 1.23 to 2.77, while higher catalyst concentrations gave rise to bimodal distributions. Our own results clearly show that the initiator homogeneity *increases* dramatically over the same catalyst concentration range. Particularly striking is the result quoted in ref 1 for the polymer prepared from the initiator containing no triethylamine. This showed a unimodal molecular weight distribution of dispersity 1.25, and with a comparatively small percentage of high molecular weight tail, yet our results indicate that the initiator in this case contains much less of the desired (IIa) than it does of polyfunctional material and unreacted sec-butyllithium.

It is difficult to imagine how such a mixture would give rise to a low dispersity polymer, but differing rates of initiation could provide an answer. Initiation by sec-butyllithium ought to occur faster than by species lithiated at a benzyl position, and it could be argued that initiation by polyfunctional material would be subject to steric hindrance in direct proportion to the degree of polymerization of the latter. Thus, a fortuitous inverse relationship between functionality and rate of initiation could lead to polymers of narrow molecular weight distribution. In the absence of experimental evidence, however, such arguments must remain speculative, and clearly more work is required to clarify this aspect of the problem.

The foregoing arguments apply with equal force to the findings of Rempp and coworkers[2] who also obtained low dispersity polymers by initiation with the *m*-diisopropenylbenzene/sec-butyllithium system. Upon treating the living polymers with divinylbenzene and with dibromo-*p*-xylene, they observed gelation and molecular weight increases respectively, but neither of these tests can distinguish an *average* functionality of two from an *exact* functionality of two.

The French workers studied the anionic polymerization of (I) and found that it proceeded smoothly at −60°C giving a polymer containing one pendant double bond per monomer unit. Copolymers of (I) with α-methylstyrene were similarly formed and on warming the living copolymers to room temperature, 'quantitative depropagation' was observed, although it is not clear whether the presence of dimers, trimers, etc., was specifically ruled out. The depropagation or otherwise of the homopolymer of (I) is not mentioned, nor is the ceiling temperature for its formation. The latter would be expected to be considerably higher than that of α-methylstyrene (5°C)[4] since T_c for the *para*-isomer of (I) has been measured[5] as 49° ± 5°C.

Another experiment performed by the French group involved addition of (I) (in an unspecified proportion) to monofunctional living polystyrene in benzene solution at 40°C. After 2 h the polymer was recovered and analysis revealed no star-shaped molecules and <5% coupled products from which it was concluded that (I) could not polymerize under these conditions. This ought to be a very sensitive test, since reaction with the polystyrene chain ends to give (V), followed by 'oligomerization' of the type we have observed should produce dramatic increases in the molecular weight of the polystyrene. However, it is open to question whether the coupling of species such as (V) can be compared with the oligomerization of (I) since in the former case, steric constraints might be more severe. Certainly, our own results show quite clearly that (I) can and does form oligomers in benzene solution at room temperature and above.


(5)

The greatest discrepancy between our results and those of Rempp and coworkers concerns the n.m.r. spectra of quenched samples of the initiator. The French group found evidence for one unreacted isopropenyl group per molecule, whereas we could not detect residual unsaturation by n.m.r. spectroscopy. The reason for this discrepancy remains a mystery, but it must be stated that the scheme proposed by Rempp, namely lithiation of one site in (I) to give (III), followed by lithiation of the second site *after* polymerization of added monomer has begun at the first site, seems highly improbable; there appears to be no reason why sec-butyllithium should react with the vinyl group in (III) to the exclusion of an added monomer present in large excess.

CONCLUSIONS

In our hands, the addition of sec-butyllithium to *m*-diisopropenylbenzene in benzene or cyclohexane does not give rise to a bifunctional anionic initiator, but instead gives a mixture of bi- and polyfunctional material, together with unreacted sec-butyllithium. The reaction is very sensitive to the presence of triethylamine in cyclohexane solution, but is less so in benzene. In the former solvent, production of polyfunctional material is all but suppressed by triethylamine at a concentration of 1.0 molecule per litio site, but according to Sharkey and coworkers[1], polymers of rather high dispersity are formed in the presence of triethylamine at this concentration.

Careful examination of the results of Sharkey[1] and Rempp[2] suggests that they too may have unwittingly experienced the same problem and although discrepancies remain, and further work is required to verify some points, the use of this sytem as a bifunctional initiator must be viewed with suspicion. A promising alternative may be provided by the addition of sec-butyllithium ot one or other of the double 1,1-diphenylethylene compounds described by Tung and coworkers[6], the reaction taking place rapidly in benzene solution in the absence of polar additives.

Finally, we recommend the use of g.p.c. as a convenient means of detecting oligomerization, and hence polyfunctionality in all systems of this type.

EXPERIMENTAL

Cyclohexane and benzene were purified by the method of Foss, Jacobson and Sharkey[1]. *m*-Diisopropenylbenzene was prepared as described by the same authors, but was purified by distillation in a spinning band apparatus (b.p. 94°C/8 mm), since distillation in a conventional low-pressure apparatus led to polymerization. Triethylamine was stored over molecular sieves and distilled prior to use; sec-butyllithium was obtained as a 1.2 M solution in cyclohexane from Aldrich Chemical Co., and was standardized by the Gilman double titration method[7].

N.m.r. spectra were recorded on a Varian HA-100 instrument for CCl_4 solutions with tetramethylsilane as internal standard. The mass spectrum was run on an AEI MS-30 instrument at 70 eV. G.p.c. was performed on a Waters M-6000A instrument equipped with two μStyragel columns (500 and 100Å) and a Model 440 UV absorbance detector, using $CHCl_3$ as a solvent at a flow rate of 0.5 ml min^{-1}.

Addition of sec-butyllithium to m-diisopropenylbenzene

Approximately 100 ml solvent was distilled into a conical flask containing a magnetic stirring bar. The flask was sealed with a rubber septum, and approximately 5 mmol *m*-diisopropenylbenzene introduced by syringe, the syringe being weighed before and after the addition. The desired amount of triethylamine was then added, followed by the calculated volume of sec-butyllithium solution, both by syringe. After overnight stirring at room temperature in the dark, the seal was removed and 30 ml water added with vigorous stirring. After the colour had discharged and effervescence had ceased, the layers were separated, the organic layer washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. (In runs 7 and 8 the flask was immersed in a water bath at 55°–60°C before adding the sec-butyllithium, then kept at this temperature for 6 h).

Distillation of the combined products of runs 3 and 4 gave a colourless, mobile oil b.p. 112°–114°C (0.1 mm).

ACKNOWLEDGEMENT

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Note added in proof

Dr Sharkey[a] has pointed out that, in their experiments, (I) was always added to preformed $BuLi/Et_3N$ complex and that this different order of mixing reagents may explain our conflicting observations. This is reasonable when addition of BuLi to diene is very fast; however, the contradictory results obtained in cyclohexane without catalyst, where the addition is very slow, are less easily reconciled in this way. Our conclusion that the product is polyfunctional when the reaction is conducted in benzene solution is supported by more recent observations[b].

[a] Sharkey, W. H. personal communication

[b] Fetters, L. J., Kamienski, C. W., Morrison, R. C. and Young, R. N. *Macromolecules* 1979, **12**, 344