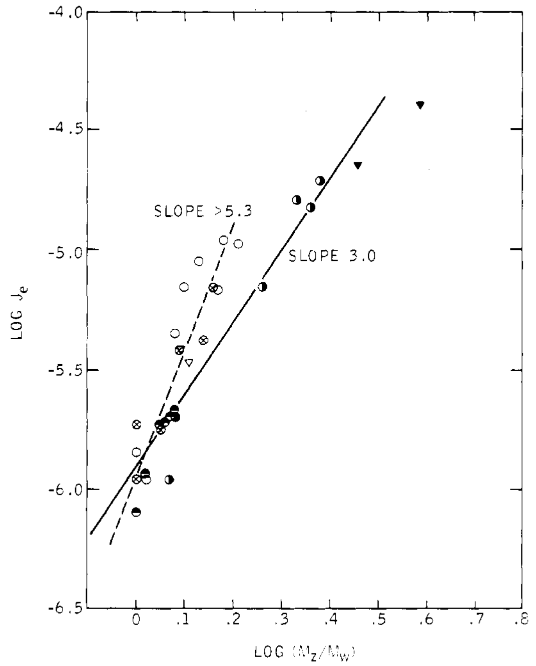

**Figure 2.** Logarithmic plot of the steady state compliance $J_e$, cm$^2$/dyn, vs. ($M_z/M_w$). See Figure 1 for data point details.

makes it a useful empirical contribution.

One of the referees is of the viewpoint that the relationship presented in this note is no better than the Kurata et al. relation (eq 8) and insisted that the bottom half of their Figure 12 (ref 11) be reproduced in the manuscript so that the reader can draw his own conclusion. In Figure 2 the ($M_z/M_w$) relationship is presented with additional data shown in Figure 1. The solid line has a slope of 3.0. The dashed line which best fits Prest and Porter and Onogi et al.'s data has a slope of more than 5.3. It can be noted that only the data of Mills and Nevin and Akovali's fall on the line of slope 3.0. As mentioned earlier in the text, Mills and Nevin had observed a slope of 3.7. The range of Akovali's ($M_z/M_w$) data is only within 20% and cannot be heavily relied upon for the critical test of such relations.

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## Remarks on Organodilithium Initiators

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The synthesis of difunctional organolithium initiators is of interest since these species offer a route for the preparation of near-monodisperse elastomeric polydienes possessing reactive groups at each chain end as a result of a controlled termination reaction,[1] e.g., the addition of ethylene oxide. These $\alpha,\omega$-polydienes (telechelic polymers) are then candidates for the preparation of model networks via the appropriate postpolymerization cross-linking reactions.

The synthesis of these organodilithium initiators has generally followed two methods, viz., (a) the generation of ion–radical species which then couple to yield the dicarbanionic initiator[2–7] and (b) the reaction of a monofunctional organolithium with an appropriate diolefinic species in the ratio of 2:1 (RLi–diolefin).[8–17] These procedures are carried out with nonpolymerizable substrates or under conditions where polymerization is suppressed.

### Discussion

A common feature of organodilithium preparations is that they have been carried out in a polar solvent or polar solvent–hydrocarbon mixture. This was done in order to enhance both the rate of initiator formation and the solubility of the resultant difunctional initiator. It has been found[3,5–7,11–16] that aromatic ethers or tertiary amines can be used as cosolvents and unlike the aliphatic ethers, for example, their presence exerts minimal influence on polydiene 1,4 microstructure.

Summarizing previous attempts to synthesize organodilithium compounds suitable as initiators of polymerization Lutz et al.[18] and Beinert et al.[19] report that a number of papers and patents describe organodilithium initiators. They assert that the molecular weight distributions of the polymers derived from some of these initiators are broad as (apparently) a consequence of slow initiation and, in the case of the polydienes, the 1,4 content is reduced by the presence of triethylamine. However, these conclusions are at variance with results presented by the original authors. For example, it is stated in ref 11 to 14 that an efficient difunctional initiator, 1,3-bis(1-lithio-3-methylpentyl)benzene, can be prepared from *sec*-butyllithium and *m*-divinylbenzene in the presence of small quantities of triethylamine. The culmination of some of the work described therein was the synthesis[11] of a poly(styrene–isoprene–styrene) triblock copolymer of high tensile strength, predictable molecular weight, and possessing diene stereochemistry little different from that obtainable on polymerization in a pure hydrocarbon solvent.

The claim that, for example, small amounts of triethylamine exert a minimal influence on polydiene microstructure is fortified by results for polybutadiene prepared by the difunctional lithium initiator prepared from, in this case, the mixed isomers of 2,4-hexadiene.[6,7] The amine–chain end ratio was about 1.2:1. These microstructure data are shown in Table I along with that for a polybutadiene prepared by *sec*-butyllithium initiation

Table I
Polybutadiene Microstructure

| sample[a] | microstructure[b] cis-1,4 | trans-1,4 | 1,2 | $M_n{}^c \times 10^{-5}$ g mol$^{-1}$ |
|---|---|---|---|---|
| 1 | 36 ± 4 | 50 ± 5 | 14 ± 2 | 0.35 |
| 2 | 30 ± 1 | 59 ± 1 | 12 ± 1 | 2.5 |
| 3 | 36 ± 3 | 54 ± 2 | 10 ± 1 | 1.5 |

[a] Samples 1 and 2 were prepared by the difunctional initiator in benzene. The polymerization temperature was 20 °C. Sample 3 was prepared by *sec*-butyllithium. [b] From infrared measurements: Dr. P. Dreyfuss, private communication. Similar results have been found for isoprene.[7,20] [c] From GPC, the $\bar{M}_z/\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ ratios from GPC for all three samples ranged from 1.03 to 1.08. The 7-column set discussed in ref 21 and 22 was used for this evaluation and for the chromatograms of Figure 1.

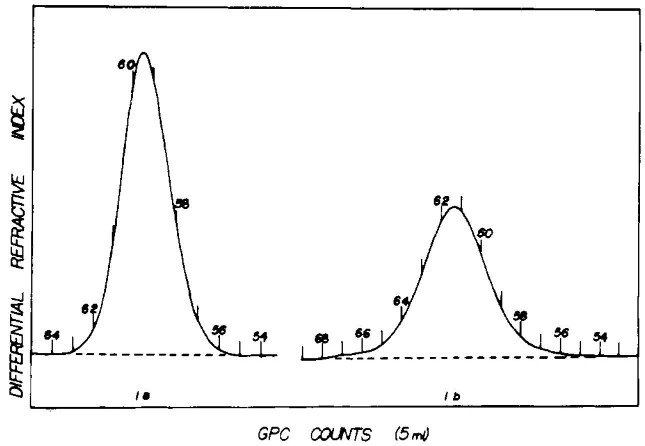


**Figure 1.** (a) Gel permeation chromatogram of polybutadiene prepared by 1,3-bis(1-lithio-3-methylpentyl)benzene: $\bar{M}_n = 1.9 \times 10^3$ (VPO); $\bar{M}_w/\bar{M}_n = 1.1_2$ (GPC). (b) Gel permeation chromatogram of CDS-B-2 polybutadiene: $\bar{M}_n = 9.5 \times 10^2$ (VPO); $\bar{M}_s/\bar{M}_n = 1.2_6$ (GPC).

in *n*-hexane. These polybutadienes were prepared under conditions[23,24] where the 1,4 microstructure is not influenced by the concentration of active chain ends.

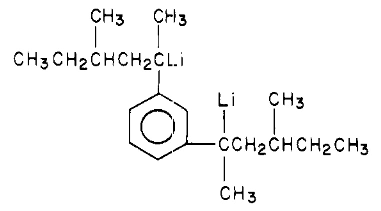
The fact that the difunctional initiator based on the 2:1 adduct of *sec*-butyllithium-*m*-divinylbenzene (95% pure) can yield polybutadiene with near monodisperse molecular weight distributions is shown in Figure 1a. The narrow and symmetrical nature of the molecular weight distribution apparent in Figure 1a is *not* an artifact due to inadequate resolution by the GPC columns. This is attested to by the chromatogram of Figure 1b which is that of a standard polybutadiene with an $\bar{M}_w/\bar{M}_n$ value of about 1.26.[25]

It should be noted that the presence of the ethyl vinyl benzene isomers in the divinylbenzene can lead to metallation reactions in a fashion similar to that observed with toluene.[26] Hence, the divinylbenzene used should be essentially free of the ethyl vinyl benzene isomers if long-term retention of the difunctional nature of the initiator is to be achieved. In the absence of the ethylvinylbenzene isomers, the 1,3-bis(1-lithio-3-methylpentyl)benzene remains soluble and is stable for at least 2 months at ambient temperature.

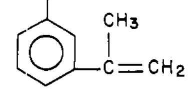
Beinert et al.[19] have further claimed that the difunctional initiator prepared[3,5,7] from 1,1-diphenylethylene and lithium dispersion in a benzene–aromatic ether medium gave rise to polymers which possessed "high polydispersity". However, the characterization data in ref 5 and 7 demonstrate that 1,1,4,4-tetraphenyl-1,4-dilithiobutane can be used to prepare both homopolydienes and triblock copolymers which possess near-monodisperse molecular weight distributions. Thus, here too there is a dichotomy between the content of the original literature and the synoptic abstract of Beinert et al.[19] It should also be noted that partial initiator insolubility will lead to the preparation of polydisperse polymer.[16,17]

These same authors report that they have successfully prepared a difunctional initiator from *m*-diisopropenylbenzene and *sec*-butyllithium in benzene solution. In contrast, Foss et al.[16] earlier reported that the same reagents in cyclohexane solution gave rise to a product which rapidly aged to an insoluble material which they proposed was an agglomerate. It is possible that the differences between the results of the two groups might be due to the use of different solvents: benzene undoubtedly having some solvating power, in contrast to cyclohexane. However, Foss et al.[16] prepared their initiator at an elevated temperature (60 °C) which is conducive to the formation of organolithium compounds of functionality greater than two.

The reaction between *sec*-butyllithium and *m*-diisopropenylbenzene (2:1 ratio) in benzene solution might be expected to yield 1,3-bis(1-lithio-1,3-dimethylpentyl)benzene (I). However, $^1$H-NMR analysis of the terminated initiator revealed[18] that the initiator solution was in fact an equimolar mixture of *sec*-butyllithium and species II, 1-(1-lithio-1,3-dimethylpentyl)(3-isopropenyl)benzene. This is an unsurprising result since it has been shown[14,15] that species II is formed cleanly in benzene in the absence of polar additives when equimolar quantities are used. (Identical results have been obtained for *m*-divinylbenzene.[15] The divinylbenzene isomers have also exhibited a notable reluctance to form the xylylene dianion adducts in benzene with styryl-, isoprenyl-, and butadienyllithium.[27,28]) In contrast, species I is cleanly formed in benzene when the *sec*-butyllithium *m*-diisopropenylbenzene ratio is 2:1 and triethylamine is present with a concentration equal to that of the *sec*-butyllithium.



I



II

In an attempt to explain the difunctional nature of their polystyrene, Beinert et al.[19] invoked the mechanism wherein the monofunctional adduct II reacted with the monomer to be followed by the *immediate* reaction of the residual *sec*-butyllithium with the pendant isopropenyl group. This step then allegedly yields the difunctional initiator. We submit that this reaction sequence, for the case of diene monomers, is highly improbable. The ratio of initiator to monomer quoted[19] is in the range of 1:100 to 1:200, and on purely statistical grounds, the reaction of the residual *sec*-butyllithium with monomer is favored over that with the pendant isopropenyl groups in approximately the same proportion. The relative lack of reactivity of these pendant groups of the meta and para isomers in anionic polymerization has been noted.[18,32]

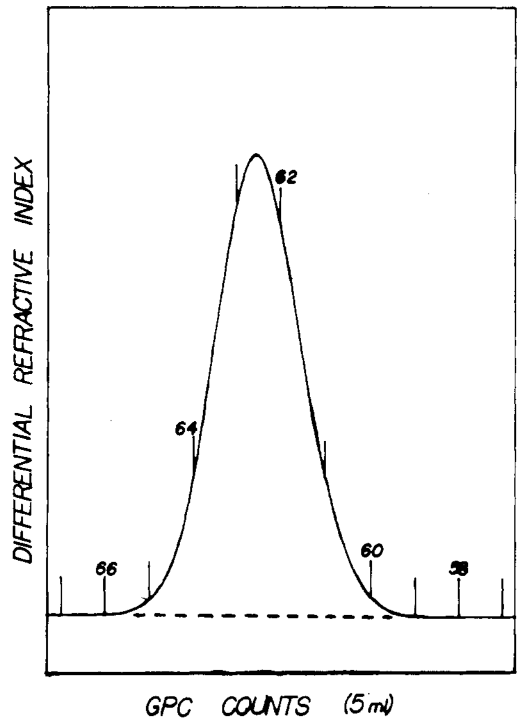


**Figure 2.** Gel permeation chromatogram of polybutadiene prepared by 1,3-bis(1-lithio-1,3-dimethylpentyl)benzene: $\bar{M}_n$ (VPO) = $2.1 \times 10^3$; $\bar{M}_w/\bar{M}_n = 1.0_6$ (GPC). The 7-column set used for this analysis had a porosity range different from that used in Figure 1 and Table I.

Thus, when the monomer used is a diene, any *sec*-butyllithium consumed by direct reaction with the same will be expected to lead to the generation of polydienyllithium which will display a marked preference for homopropagation over crossover with either the pendant in-chain styrenoid[33-35] (from divinylbenzene) or the isopropenyl residues. Spectroscopic measurements we have done show that the reaction of isoprenyllithium with $\alpha$-methylstyrene in benzene (at 20 °C) is *markedly* slower than the corresponding reaction involving styrene.

The consequence of this "belated" reaction of the pendant isopropenyl group is that, at least for dienes, nonlinear chains were doubtlessly formed in the systems of ref 18 and 19. These species could resemble unsymmetrical three-armed stars and other types of branched chains.

Lutz et al.[18] and Beinert et al.,[19] in an attempt to demonstrate the linearity of the polystyrenes prepared with their initiators, measured $\langle S^2 \rangle$ for these polymers after chain extension and compared these values with those calculated from the relation[33] $\langle S^2 \rangle^{1/2} = 9.45 \times 10^{-2}\, M^{0.635}$. This relation is derived from a series of near-monodisperse polystyrenes whereas the samples of Lutz et al.[18] and Beinert et al.[19] were, as a consequence of the post-polymerization chain extension reaction, polydisperse. Hence, since $\langle S^2 \rangle$ is a z-average molecular weight dependent parameter, a meaningful comparison of $\langle S^2 \rangle$ values can only be made for polystyrenes of similar polydispersities.

We also wish to note that the difunctional initiator prepared from *sec*-butyllithium and *m*-diisopropenylbenzene with triethylamine present (*sec*-butyllithium–amine ratio of 1:1) will yield near-monodisperse low molecular weight polybutadiene. An example of this is shown in Figure 2.

Certain attributes needed by organodilithium initiators are apparent. First, the initiator must possess carbon–lithium bonds of equal reactivity; second, the initiator must be completely soluble in hydrocarbon media; and third, the initiator must initiate the polymerization reaction swiftly, relative to the subsequent propagation step. Our combined experience demonstrates that 1,1,4,4-tetraphenyl-1,4-dilithiobutane, 1,3-bis(1-lithio-3-methylpentyl)benzene, 1,3-bis(1-lithio-1,3-dimethylpentyl)benzene, and the difunctional adducts from the 2,4-hexadiene isomers are organodilithium initiators which meet the foregoing criteria. The species have also shown satisfactory stability in the absence of chain transfer agents such as toluene or the isomers of ethylvinylbenzene.

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