Hydrocarbon-Soluble Di- and Multifunctional Organolithium Initiators

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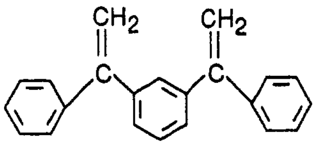
ABSTRACT: Soluble difunctional organolithium initiators were prepared by the addition of oligomeric poly(styryllithium) to stoichiometric amounts of double 1,1-diphenylethylene (DDPE) compounds: bis[4-(1-phenylethenyl)phenyl] ether; 1,4-bis(1-phenylethenyl)benzene, and 4,4′-bis(1-phenylethenyl)-1,1′-biphenyl. The resulting products of this addition reaction were soluble in benzene and were capable of initiating diene polymerization. A reversal was detected at the end of the addition reaction to one of the three DDPE compounds, bis[4-(1-phenylethenyl)phenyl] ether. The diphenyl ether group in bis[4-(1-phenylethenyl)phenyl] ether, which might have reacted with poly(styryllithium) to cause a shift of equilibrium, was suspected to be the cause of the anomaly. The styrene–butadiene–styrene triblock copolymer prepared from these difunctional initiators gave narrow and symmetrical chromatograms by GPC. The tensile strength of the block copolymers, however, was low. A potential route of preparing soluble organolithium initiators with functionality higher than 2 was demonstrated.

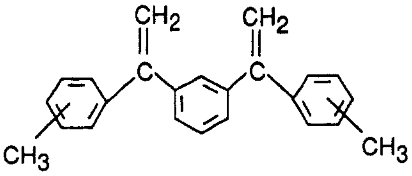
Introduction

Development of an ideal difunctional organolithium initiator, usable in hydrocarbon solvents for the anionic polymerization of diene monomers, has been a continuing effort since the late 1960s. Because of the strong association of organolithium compounds, most of the dilithium initiators require some amount of polar additives to make them soluble in hydrocarbon solvents. The first published dilithium initiators[1] with significant solubility in hydrocarbon solvents without the use of any polar additive were prepared by the reaction of *sec*-butyllithium with two particular double 1,1-diphenylethylene (DDPE) compounds, PEB and MPEB. These initiators were used later to prepare unique telechelic polybutadienes[2] and block copolymers.[3] Earlier,[4,5] we had prepared other dilithium initiators based on four different DDPE compounds (I–IV).



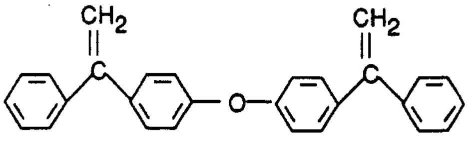
PEB

1,3-di(1-phenylethenyl) benzene



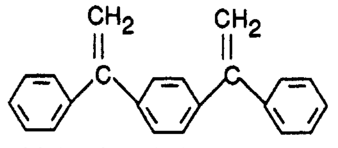
MPEB

1,3-di[1-(methylphenyl)ethenyl)] benzene



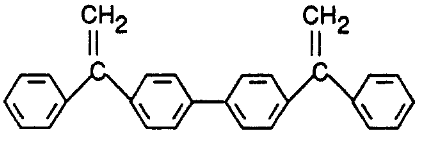
(I)

Bis[4-(1-phenylethenyl)phenyl]ether



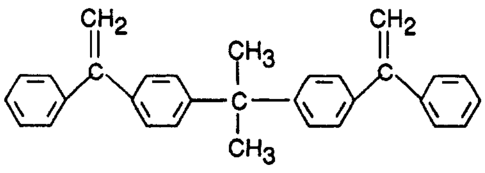
(II)

1,4-bis(1-phenylethenyl)benzene



(III)

4,4'-bis(1-phenylethenyl)-1,1'-biphenyl



(IV)

2,2'-Bis[4-(1-phenylethenyl)phenyl]propane

The addition reactions of these four compounds with *sec*-butyllithium were found to be clean and rapid. The resulting initiators were insoluble, but when freshly prepared, they were fine suspensions and would coagulate into hard particles only upon standing for several hours or more. The fine suspensions were effective in initiating

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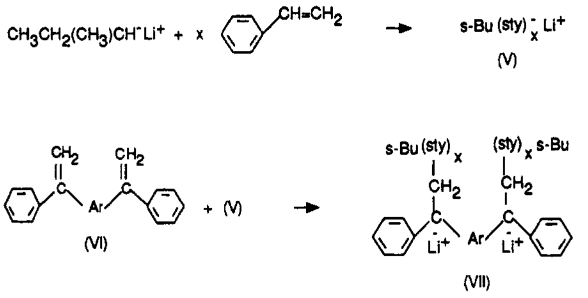
butadiene polymerization and became soluble shortly after contacting the monomer. They could also be made soluble by reacting the suspensions with a small amount of isoprene or butadiene. In either case, polar additives were not required. When oligomeric poly(styryllithium) was used in place of *sec*-butyllithium, the initiators prepared had direct solubilities in hydrocarbons without any polar additives. These reactions and the resulting initiators were briefly outlined in patent[6] literature. In this paper, a full account of this investigation is presented.

Our interest in presenting the full account of this investigation now is prompted by the recent activities on the reaction of poly(styryllithium) with DDPE compounds. Quirk et al.[7,8] used the adduct of poly(styryllithium) with PEB to prepare novel star-shaped block copolymers. Since the initiators prepared by the reaction of oligomeric poly(styryllithium) with DDPE compounds **I**–**III** were discovered before the soluble dilithium initiators derived from PEB and MPEB, they could be the first dilithium initiators that had direct solubility in hydrocarbons. As will be shown later in this paper, the reaction of poly(styryllithium) with DDPE compounds has also the potential of preparing soluble organolithium initiators of functionality higher than 2.

The kinetics of poly(styryllithium) addition to DDPE compounds **I**–**III** have been carefully studied by Yamagishi et al.[9] The investigation to be presented in this paper centered mainly on the utility of the reaction to prepare soluble di- and multifunctional initiators. The reaction was conducted in solutions of 1–2 orders of magnitude more concentrated than those studied by Yamagishi et al.

Results and Discussion

Soluble Dilithium Initiators (DLIs). The scheme for preparing soluble DLIs is as follows:



If "Ar" is diphenyl oxide, then DDPE compound **VI** is **I**. The degree of polymerization, x, of the poly(styryllithium) oligomer at the right-hand side of the first equation represents an average quantity.

Since a larger organodilithium molecule might have a greater solubility, the aimed value of x in the first experiment was 20. The DDPE compound was **I**. The poly(styryllithium) was prepared in benzene at room temperature at a concentration of about 4×10^{-2} M. The orange poly(styryllithium) solution changed rapidly to deep red when a benzene solution of a stoichiometrical amount of compound **I** was added. No precipitation was observed after 24 h. The progress of the reaction was followed by the withdrawal of aliquot amounts of the reacting solution which were quenched with acetic acid and analyzed by GPC. Figure 1 shows six of the GPC chromatograms. The first chromatogram was the quenched poly(styryllithium) oligomer. The peak had a molecular weight of 2350 which corresponded roughly to $x = 21$. The other chromatograms had two peaks—one at a molecular weight of 3190 and the other at a molecular weight of 5790 in polystyrene scale. They corresponded to the monoadduct and the diadduct of the reaction, respectively. Revealed by the chromatograms was a surprise reversal of reaction at the later stages of the reaction. The size of the diadduct peak reached a maximum between 2 and 4 h and then slowly decreased. The monoadduct peak made a corresponding decrease and then increased. The efficiency of the GPC column was insufficient to separate the polystyrene oligomer peak from the monoadduct peak; thus, it is unclear whether both the poly(styryllithium) and the monoadduct reappeared in the reverse reaction.

Three more runs were made using DDPE **I** and poly(styryllithium) of $x = 10$, 5, and 2.5. The reactions appeared to proceed similarly, and no precipitates were formed in all three runs after 24 h. No aliquot samples were taken during these runs for GPC analysis. A portion of the DLIs made with poly(styryllithium) of $x = 10$ was quenched at 48 h. As shown in Figure 2, the monoadduct peak in this sample was larger than that in the 24-h sample in Figure 1, indicating that given enough time the diadduct peak might disappear completely. This reversal was not observed by Yamagishi et al.[9] in their spectroscopic study of the same reaction at concentrations about 1 order of magnitude more dilute. In Yamagishi et al.'s study, either a large excess of poly(styryllithium) or a large excess of DDPE was used. It is possible that only when the reactants are at near stoichiometric amounts would the reverse reaction be detectable.

The DLI made with poly(styryllithium) of $x = 2.5$ was used to make a styrene–butadiene–styrene (SBS) triblock copolymer. Benzene was the polymerization solvent. Styrene was added after the completion of butadiene polymerization. The recovered SBS had good elongation, 1063%, but the tensile rupture strength was only 1360 psi. The effect of the reverse reaction undoubtedly influenced the purity of the triblock and contributed to the low rupture strength.

Finally, the reaction between a poly(styryllithium) of minimum x, $x = 1$, and **I** was carried out. Again no precipitate was observed after 3 h. The difunctionality of the initiator was verified by a gelation test described by Farrar.[10] The initiator in question was used to polymerize a small amount of isoprene, and then a stoichiometrical amount of silicon tetrachloride was added to couple the poly(isoprenyllithium). If the initiator was monofunctional, the product would remain in solution as star-shaped branched molecules. If it was difunctional, infinite molecular weight gel would form. When the sample above was tested, gelation occurred, showing that the soluble product was principally difunctional. The test was also carried out for the 24-h sample of the $x = 21$ run. Gelation formed again in the test, indicating that despite the existence of the reverse addition reaction, the principal product was still difunctional. Table 1 summarized the two gelation tests.

For a reaction reversal to take place, there must be a slow side reaction removing one or more of the reactants to offset the equilibrium state based on the original concentrations of the reactants. The reactants for the present reaction are poly(styryllithium) and DDPE **I**. Since poly(styryllithium) is a stronger base than the diadduct DLI, slow reacting impurities in the reaction mixture or

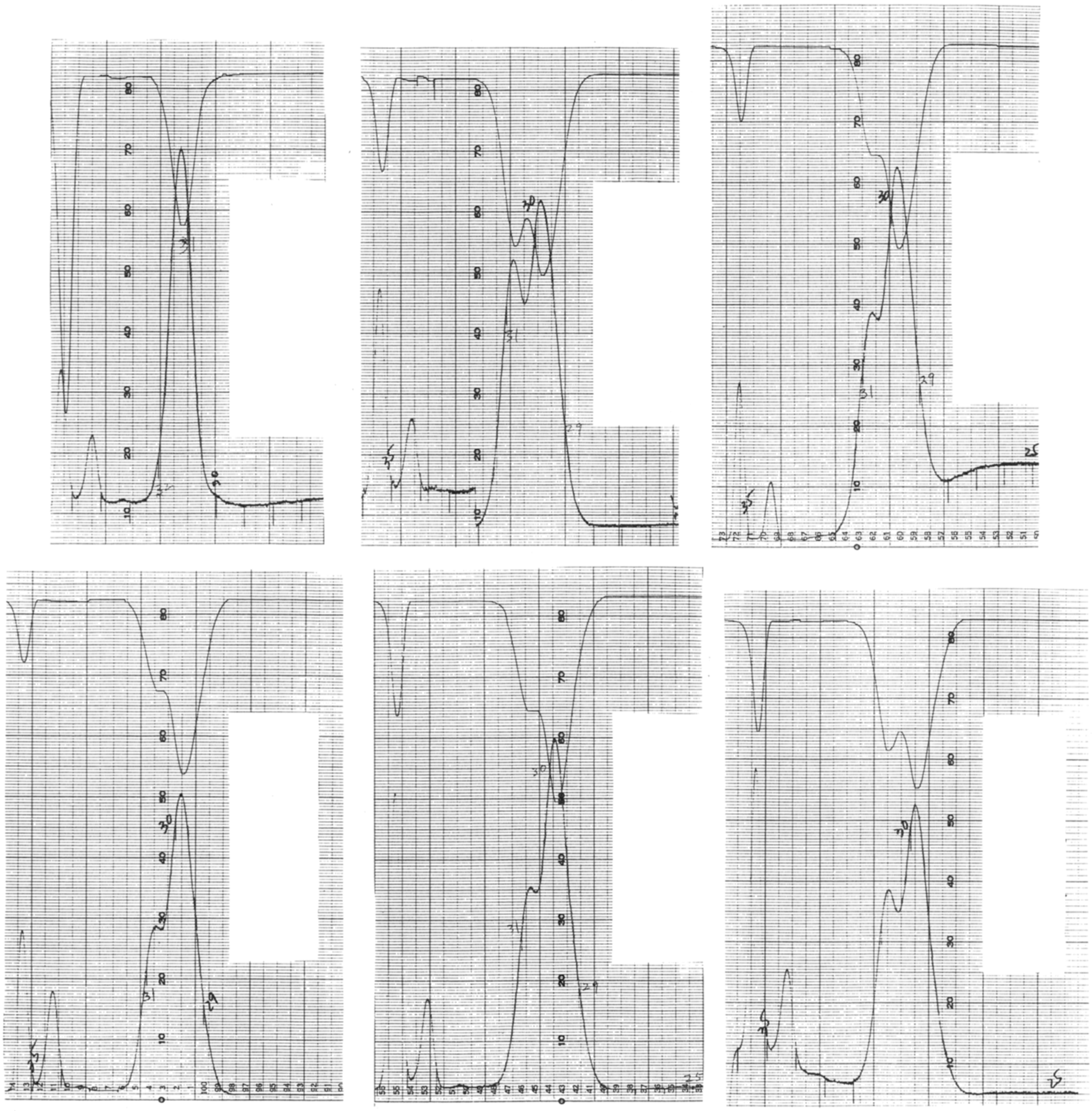


Figure 1. GPC chromatograms of products formed at various times between poly(styryllithium) (**V**) with a DP of 21 and DDPE **I**. The upper curve was the chromatogram from the UV detector and the lower curve from the differential refractive index detector. At the extreme left is the solvent peak. (top left) PS oligomer, (top middle) 1 h, (top right) 2 h, (bottom left) 4 h, (bottom middle) 6 h, (bottom right) 24 h.

from a slow leak of the apparatus would react faster with poly(styryllithium) and cause a shift in the equilibrium. A repeat run with poly(styryllithium) of $x = 5$ was made with special attention to the purity of the reactants and the tightness of the apparatus. In this run, the diadduct maximum was higher and was reached in only about 1-h reaction time. The reverse reaction was also faster. At 23 h, the monoadduct peak was much higher than that at 24 h in Figure 1 and was similar to that shown in Figure 2 at 48 h. It is therefore unlikely that impurities were the source of the reaction reversal.

Another possible cause for the reaction reversal was the quenching of poly(styryllithium) by DDPE **I** itself. A run using DDPE **II** to replace **I** and another run using **III** were made. No reversal of the reactions was in evidence. In the case of DDPE **II**, the rate of diadduct formation was comparable to that for **I**. In agreement with the findings of Yamagishi et al.,[9] the addition of poly(styryllithium) to DDPE **III** was faster. The addition reaction was essentially complete in about 30 min. The absence of reaction reversals strongly suggests that the diphenyl ether group in **I** was responsible for the quenching of poly(styryllithium) and thus offsets the equilibrium.

Soluble Multifunctional Initiators. Yamagishi et al.[9] found that when diadduct **VII** was mixed with styrene monomer, polystyrene grew only from one end and compound **VIII** should be the principal product. They found also that for DDPE compounds **II** and **III**, the first double bond reacted with poly(styryllithium) much faster

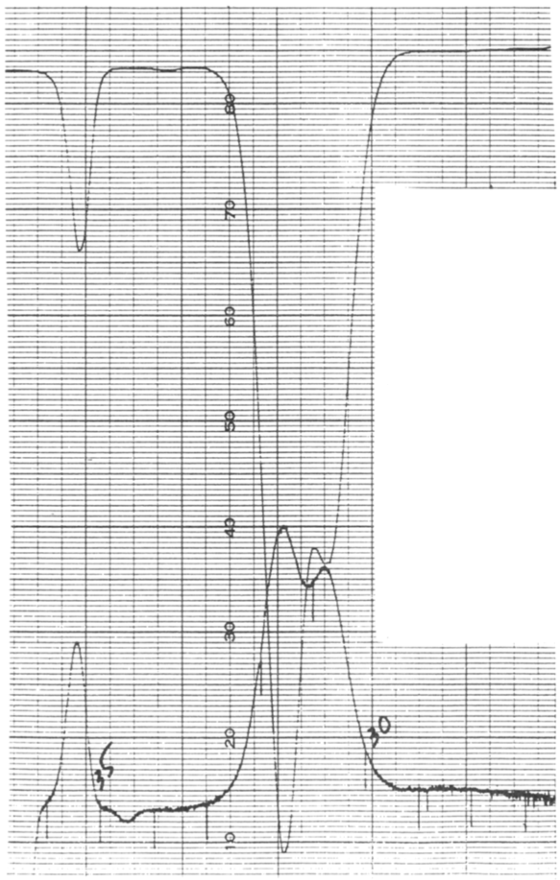
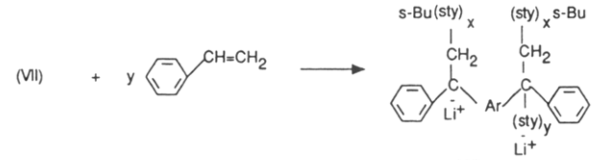


Figure 2. GPC chromatogram of the product after 48 h of reaction between poly(styryllithium) (V) with a DP of 10 and DDPE I. The upper curve was the chromatogram from the UV detector and the lower curve from the differential refractive index detector. At the extreme left is the solvent peak.

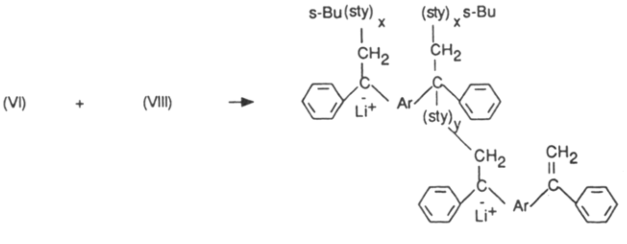
Table 1. Gelation of Initiators Formed by the Reaction of Polystyrene Oligomer with DDPE I

run	*x* in oligomer	DLI, mequiv	DLI reaction time, h	isoprene, g	$SiCl_4$, mequiv	gel, %
8868-28	20	0.50	24	3.4	0.52	70
8868-33	1	1.15	3	6.8	1.12	78

than the second double bond. If **VIII** is allowed to react with a mole of **VI**, then **IX** should be the principal product.

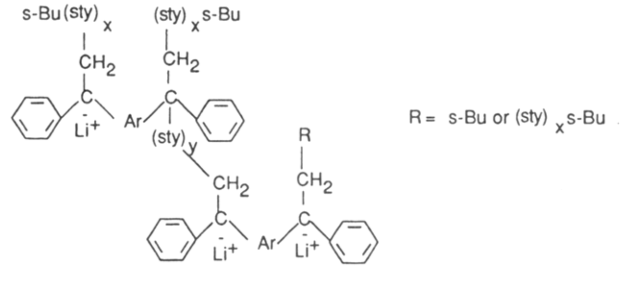


(VIII)

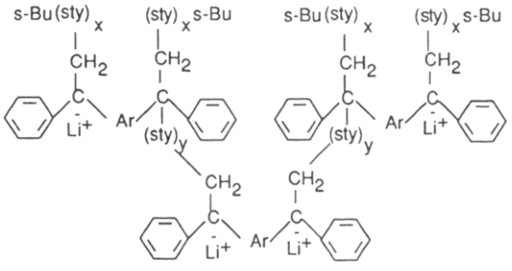


(IX)

Reacting **IX** with another mole of *sec*-butyllithium or **V** should yield a trifunctional organolithium compound (**X**). Reacting **IX** with another mole of **VIII** should give a tetrafunctional organolithium compound (**XI**). These multifunctional compounds could be useful initiators.

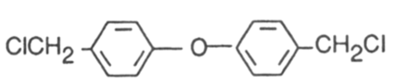


(X)



(XI)

Compound **XI** with diphenyl oxide as Ar, $x = 1.5$ and $y = 11$, was prepared in benzene solution, from its precursor compound **VII**. After converting **VII** to **VIII**, **VI** in one-half the mole amount of **VIII** was added to give **XI** directly. The multifunctionality of the product was verified by a gel test slightly different than the one used before. The product in question was used to initiate a small amount of isoprene as in the earlier test. To this solution containing approximate 0.48 mmol of the material, 0.35 mmol of bis-[4-(1-chloromethyl)phenyl] ether **XII** in benzene was added. Gelation set in immediately. Compound **XII** is difunctional. When **XII** was added to a similar isoprenyl anion solution prepared directly from the difunctional precursor compound **VII**, no visible gel formed. Only multifunctional anions can be gelled in contact with **XII**. Compound **XI**, therefore, may be the principal component in the product.



(XII)

It is easy to conceive that **XI** can be allowed to react again with a small amount of styrene, and the process is repeated to obtain soluble organolithium initiators of even higher functionalities.

Comparison of Styrene–Butadiene–Styrene (SBS) Triblock Copolymers. An SBS copolymer with poor tensile properties was prepared earlier using a DLI in which the reverse reaction had progressed substantially. Three more SBS copolymers were therefore made using SLIs prepared in 1 h 45 min to see if better tensile properties might be obtained. Comparison with SBS copolymers made with DLIs derived from *sec*-butyllithium is given in Table 2.

In Table 2, SBS copolymers prepared by initiators derived from poly(styryllithium) are lower by about 1000 psi in rupture strength than the corresponding SBS copolymers prepared by initiators derived from *sec*-butyllithium. The GPC chromatograms of five of the six SBS samples were monomodal and narrow in distribution. The exception was the distribution for sample 4 which was still monomodal but had a bulge on the higher molecular weight side of the peak. Sample 4 was prepared with a DLI suspension directly. The shapes of the

Table 2. Properties of SBS Triblock Copolymers[a]

	DLI precursors					
sample	DDPE	organo Li	styrene, wt %	0.001MW	tensile rupture, psi	ult elongatn, %
1	I	V	31	99	2040	1080
2[b]	I	*s*-BuLi	34	120	3200	920
3	II	V	34	95	1630	1010
4[c]	II	*s*-BuLi	36	95	2580	1010
5	III	V	33	82	1610	1030
6[b]	III	*s*-BuLi	34	76	2570	1100

[a] x in V was 2.5, and the reaction time between V and the DDPE compound was 1 h 45 min. [b] DLI suspension solubilized by contacting with isoprene before use. [c] DLI suspension used directly.

chromatograms could not have accounted for the differences in tensile properties. The chromatogram of sample 5 was as symmetrical and narrow as that of sample 2 and yet the tensile strength of the former was only one-half of the latter. Sample 4 with the broadest distribution had about the same strength with other SBS copolymers made with *sec*-butyllithium-derived DLIs. Without a more detailed study, it is difficult to arrive at an explanation of the low tensile properties of samples prepared with poly(styryllithium)-derived DLIs.

Experimental Section

DDPE compounds I and III were prepared by the procedures described by Neville and Rosser.[11] Compound II was prepared by the method given by Höcker and Lattermann.[12] Reaction of DDPE with poly(styryllithium) and preparation of SBS block copolymers were carried out under nitrogen purge at atmospheric pressure. The purging nitrogen was allowed to bubble through a sodium–naphthalene in tetraglyme solution to remove traces of moisture and oxygen. The procedures and apparatus used were essentially the same as those described earlier.[5]

A Waters Model 200 unit was used for the GPC measurements. The column consisted of four 4-ft sections packed with Styragel as was described in an earlier publication.[13]

Conclusions

By reacting an oligomeric poly(styryllithium) of average degree of polymerization as low as 1 with stoichoimetrical amounts of DDPE compounds, hydrocarbon-soluble difunctional organolithium initiators were prepared. A soluble tetrafunctional organolithium initiator was prepared by contacting the difunctional initiator with styrene monomer and then reacting again with a DDPE compound. Soluble initiators of even higher functionality potentially can be prepared by repeating the process one or more times.

A reversal of the addition reaction was observed when the DDPE compound was **I**. The diphenyl ether group in **I** was the probable cause for the reaction reversal, as the addition reaction involving compounds **II** and **III** did not undergo the same reversals.

The SBS triblock copolymer prepared by these soluble initiators had a tensile strength about 1000 psi lower than the SBS copolymer made by initiator prepared from reacting *sec*-butyllithium with the same DDPE compounds. The GPC chromatograms of these SBS polymers did not show any anomalies that could explain the differences in tensile properties.

References and Notes

(1) Tung, L. H.; Lo, G. Y.-S.; Beyer, D. E. European Patent Application 0,001,977, 1979, U.S. Patent 4,172,100, 1979; U.S. Patent 4,196,154, 1980.

(2) Tung, L. H.; Lo, G. Y.-S.; Griggs, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1551.

(3) Tung, L. H.; Lo, G. Y.-S. In *Advances in Elastomers and Rubber Elasticity*; Lal, J., Mark, J. E., Eds.; Plenum Press: New York, 1986; p 129.

(4) Tung, L. H.; Lo, G. Y.-S.; Rakshys, J. W.; Beyer, D. E. German Patent Publication DE 2634391, 1977.

(5) Tung, L. H.; Lo, G. Y.-S.; Beyer, D. E. *Macromolecules* **1978**, *11*, 616.

(6) Tung, L. H.; Lo, G. Y.-S. U.S. Patent 4,182,818, 1980; U.S. Patent 4,196,153, 1980.

(7) Quirk, R. P.; Ignatz-Hoover, F. In *Recent Advances of Anionic Polymerization*; Hogen-Esch, T. E., Smid, J., Eds.; Elsevier: New York, 1987; p 393.

(8) Quirk, R. P.; Lee, B.; Schock, L. E. *Makromol. Chem., Macromol. Symp.* **1992**, *53*, 201.

(9) Yamagishi, A.; Szwarc, M.; Tung, L. H.; Lo, G. Y.-S. *Macromolecules* **1978**, *11*, 607.

(10) Farrar, R. C. U.S. Patent 3,734,973, 1973.

(11) Neville, R. G.; Rosser, R. W. *Makromol. Chem.* **1969**, *123*, 19.

(12) Höcker, H.; Lattermann, G. *Makromol. Chem.* **1972**, *158*, 191.

(13) Tung, L. H.; Runyon, J. R. *J. Appl. Polym. Sci.* **1973**, *17*, 1589.