New perfectly difunctional organolithium initiators for block copolymer synthesis: Synthesis of dilithium initiators in the absence of polar additives

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New types of difunctional organolithium initiators have been prepared by addition of sec or tert-butyl lithium on two families of non polymerizable precursors having two non-conjugated double bonds. They were made in pure hydrocarbon solvents such as n-hexane, the dilithium adducts being insoluble and easily purified by elimination of monofunctional species. However, they easily initiate the polymerization of monomers such as conjugated dienes, giving soluble and stable difunctional living polymers in the complete absence of any polar additive.

INTRODUCTION

One major family of thermoplastic elastomers comprises copolymers of styrene with a conjugated diene monomer[1,2], two main types being commercialized: triblock copolymers of ABA type with an elastomeric central block and rigid end blocks or starshaped copolymers with rigid end blocks. The three methods generally used for synthesis are sequential monomer addition, synthesis of AB diblocks that are then coupled, and successive polymerization of diene and styrene starting from a difunctional initiator.

The successive formation of the three blocks necessitates high purity conditions and the formation of a monodisperse third block has been found difficult to achieve[3]. The coupling method is at present the most used for styrene–butadiene and styrene–isoprene copolymers (triblocks by Shell[4], star copolymers by Phillips Petroleum[5]) but has several drawbacks. One is the formation of significant quantities of diblocks that have been shown to be detrimental to the mechanical properties of the thermoplastic elastomers[6]. However, these two methods are not appropriate to prepare ABA block copolymers when the first living polymer corresponding to the rigid block (poly acrylic, polylactone) does not initiate the second monomer (diene) or when block A has a low ceiling temperature (poly α-methylstyrene).

The third method using difunctional initiators is, in principle, the most general and this explains why a large number of patents and papers have claimed the preparation of difunctional initiators, and particularly of organolithium initiators that may give the highest percentage of *cis*-1,4 units (with isoprene) or of *cis* and *trans*-1,4 units (with butadiene) leading to optimal elastomeric properties.

Difunctional initiators may be prepared by two general methods, one involving the coupling of radical anions and the other using a precursor having two reactive double bonds which are reacted with a monofunctional organolithium compound. One of the first examples of radical anions coupling was given by Morton *et al.*[7] who prepared the dimer of 1,1-diphenyl ethylene (DPE) with a fine dispersion of lithium in a hydrocarbon solvent containing from 15% to 50% anisole[8]. A similar process forming α-methylstyrene oligomers has been studied more recently by Gehrke *et al.*[9] They reacted α-methylstyrene in the presence of anisole with a very fine dispersion of lithium in toluene at a higher temperature ($\sim 70°C$) but difunctionality was not demonstrated.

The direct dimerisation of radical anions of dienes is also interesting where dilithio compounds were obtained by oligomerization of isoprene[10] and 2,4-hexadiene[8] in the presence of a polar additive. The first compounds (Di Li-1 of Lithium Corporation) were prepared in dimethylether[11,12]. Values found for the difunctionality were in the range of 94–98% for freshly prepared solutions but decomposition may convert the dilithio compound adduct to a monolithio compound[10]. In the case of hexadiene[8], the use of triethyl amine was required to obtain a high concentration of active species.

Difunctional isoprenyllithium was also synthesized in non-polar solvents without any addition of polar additive[14] but precise control of the molecular weights of the polymer formed was not possible[15].

The most recently used initiators have been obtained by adding a monolithium initiator to a precursor having two reactive double bonds, and the method we have used is based on this principle. The precursor should have non conjugated double bonds reacting independently and a high ceiling temperature, in order to avoid its polymerization on the most reactive double bond (as may

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occur with 1,4-divinylbenzene). 1,3-Divinylbenzene has been proposed[16–18] but some homopolymerization of the precursor is possible and gives oligomers of higher functionality[18]. The use of 1,3-diisopropenylbenzene, having a low ceiling temperature, may prevent polymerization and has been proposed recently by several groups[15,19–22].

The use of 1,3-diisopropenylbenzene reacting, for example, with the secbutyllithium leads, however, to several difficulties. An exact stoichiometry of the reagents should be achieved, and reaction is slow in the absence of polar additives[22]. By reacting at 60°C, to accelerate the reaction, an insoluble product precipitates. When some additives, such as tertiary amines are used, the fixation of butyllithium is much faster, the initiator may remain soluble and stable until isoprene is added in order to give seeds having better stability. However, $\overline{M}_w/\overline{M}_n$ of 1.27 to 1.42 were obtained[22]. In the presence of a higher concentration of tertiary amine, trilithium initiators may be formed by reaction of the difunctional initiator with the monolithium adduct[23].

In the absence of polar additives precipitation of the dilithium compound occurs and it is then a very poor initiator[22]. Also, in order to avoid polymerization of the precursor, a sufficiently high temperature should be used, e.g. 40°C.[15] It has also been claimed that in the absence of a polar additive the reaction is incomplete and that on the average only about one double bond of the monomer has reacted. On addition of a diene (above 30°C) difunctional polymers could apparently be obtained[15] but the structures of these polymers have not been established yet and they might be branched. However, Cameron *et al.*[24] found that the reaction of 1,3-diisopropenylbenzene with sec-butyllithium in benzene or cyclohexane does not give a difunctional initiator (even at 55°C), but a mixture of di- and poly-functional material. These authors also obtained, in the presence of triethylamine, a faster reaction but the products were similar, and they concluded that the use of systems based on 1,3-diisopropenylbenzene as difunctional initiators must be viewed with suspicion. In a recent review[25], Richards came to a similar conclusion.

Another type of dilithium initiator was recently proposed by Tung *et al.*[26] These compounds were prepared by addition of sec-butyllithium on a compound containing 1,1-diphenylethylene units in benzene solution in the absence of polar additives. Low molecular weight seeds were prepared in order to obtain a narrow distribution. A similar type of initiator was described quite recently[27].

But it should be said that when polymers were described, the only evidence for success was often based only on the existence of a single peak in g.p.c. and that a comparison was not made between the experimental and the calculated values of molecular weight.

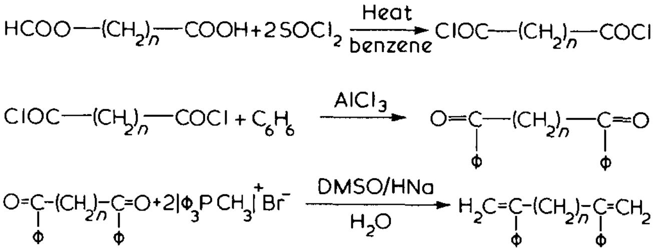
Prior to the controversies concerning 1,3-diisopropenylbenzene, we described in preliminary reports the synthesis of new types of dilithium initiators that have been isolated and that may be used without polar additives, giving perfectly difunctional polydienes and the corresponding triblock copolymers[28–31]. We used such initiators in an attempt to further initiate monomers (such as ethylene), the active centre of which may give transfer reactions in the presence of polar additives. These initiators are fully described in the present paper and are formed by reacting a precursor with butyl lithium (e.g. sec- of tert-Bu Li) generally in excess, which gives an insoluble dilithium adduct that may be washed to eliminate monofunctional derivatives. The main advantage of these initiators, besides their perfect difunctionality, is that they are quite stable. They initiate easily (in heterogeneous phase) the polymerization of butadiene or isoprene in a non-polar solvent, giving first a seed and then polymers with narrow distributions that may be either functionalized or used for the synthesis of block copolymers.

SYNTHESIS OF THE PRECURSORS

The precursors belong to two series, one with phenyl side-groups and the other with the phenyl groups in the main chain. They do not hompolymerize at the temperarures used. The double bonds are not conjugated together in order to have the same reactivity and are reactive enough to react with butyllithium in hydrocarbon solvents in the absence of any additive.

Synthesis of α,ω-bis (phenyl vinylidenyl) alkanes

These compounds are syntheized to the following scheme:



$$\mathrm{HCOO{-}(CH_2)_n{-}COOH + 2\,SOCl_2 \xrightarrow[benzene]{Heat} ClOC{-}(CH_2)_n{-}COCl}$$

$$\mathrm{ClOC{-}(CH_2)_n{-}COCl + C_6H_6 \xrightarrow{AlCl_3} O{=}\underset{\Phi}{C}{-}(CH_2)_n{-}\underset{\Phi}{C}{=}O}$$

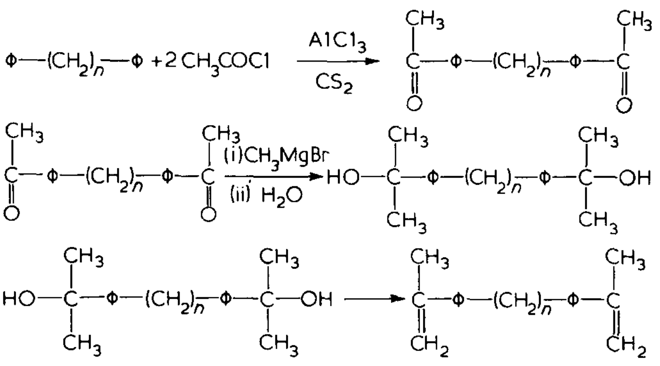
$$\mathrm{O{=}\underset{\Phi}{C}{-}(CH_2)_n{-}\underset{\Phi}{C}{=}O + 2|\Phi_3\overset{+}{P}CH_3|\overset{-}{Br} \xrightarrow[H_2O]{DMSO/HNa} H_2C{=}\underset{\Phi}{C}{-}(CH_2)_n{-}\underset{\Phi}{C}{=}CH_2}$$

A Wittig reaction modified according to Corey[32] was preferred to a method involving Grignard reagents because only vinylidenic double bonds are obtained (lack of isomers formed through the diol dehydration). In the case where n is equal to 8, 2,11-diphenyl 1,11 dodecadiene was obtained with yields for the successive reactions respectively equal to 100%, 80% and 50% (see Experimental section). 2,7-diphenyl 1,7 octadiene ($n=4$) was also prepared with nearly the same yields.

Synthesis of α,ω diisopropenyl diphenyl alkanes

This type of compound was already known[33] but had not been used as a precursor for the preparation of difunctional initiators.

In this case, it is possible to syntheize the diol through Grignard reaction and the diene is obtained by dehydration according to the following scheme:



$$\mathrm{\Phi{-}(CH_2)_n{-}\Phi + 2\,CH_3COCl \xrightarrow[CS_2]{AlCl_3} \overset{CH_3}{\underset{O}{C}}{-}\Phi{-}(CH_2)_n{-}\Phi{-}\overset{CH_3}{\underset{O}{C}}}$$

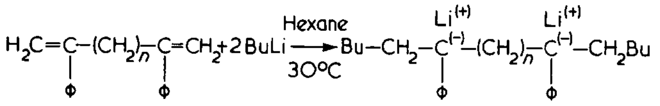
$$\mathrm{\overset{CH_3}{\underset{O}{C}}{-}\Phi{-}(CH_2)_n{-}\Phi{-}\overset{CH_3}{\underset{O}{C}} \xrightarrow[(ii)\ H_2O]{(i) CH_3MgBr} HO{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\Phi{-}(CH_2)_n{-}\Phi{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH}$$

$$\mathrm{HO{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\Phi{-}(CH_2)_n{-}\Phi{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH \longrightarrow \overset{CH_3}{\underset{CH_2}{C}}{-}\Phi{-}(CH_2)_n{-}\Phi{-}\overset{CH_3}{\underset{CH_2}{C}}}$$

To prepare stable carbanionic species, *n* must be equal or superior to two, because transfer reactions may occur if *n* is equal to 1 (acidity of benzylic atoms). For $n=2$ the yields for this series of reactions were 65%, 55% and 83% respectively.

SYNTHESIS OF DIFUNCTIONAL INITIATORS

The addition of butyllithium onto the precursors has been made under vacuum with carefully purified reagents, as is usual for anionic polymerizations. One example is given in the following equation:



$$H_2C{=}\underset{\Phi}{\underset{|}{C}}{-}(CH_2)_n{-}\underset{\Phi}{\underset{|}{C}}{=}CH_2 + 2\,BuLi \xrightarrow[30^{\circ}C]{Hexane} Bu{-}CH_2{-}\underset{\Phi}{\underset{|}{\overset{Li^{(+)}}{C^{(-)}}}}{-}(CH_2)_n{-}\underset{\Phi}{\underset{|}{\overset{Li^{(+)}}{C^{(-)}}}}{-}CH_2Bu$$

Tertiary or secondary butyllithium may be used indifferently. n-BuLi was not used since it has a lower reactivity and is difficult to purify.

When sec- or tert-BuLi are added in stoichiometric amount to diphenyl-2,7 octadiene-1,7 in hexane, the reaction is slow. After a week at room temperature, the mixture appears as a red orange solution with a maximum at 335 nm similar to that of α-methylstyryl lithium in cyclohexane. A maximum corresponding to the double bonds which did not react, may also be seen at 240 nm. No change in the intensity of the two maxima was observed after several weeks. It may be concluded that the carbanions formed do not add to the remaining double bonds. This last observation is in agreement with results of J. Furukawa *et al.*[34] concerning the attempted cyclopolymerization of α,ω-bis (4-vinylphenyl) alkane by an anionic initiator. With a molar ratio of 2 BuLi for one diene, reaction is incomplete and the concentration of precipitated dilithium compound remains low.

To enhance the reactivity, an excess of BuLi was generally added but in the case of the more reactive sec-BuLi, a ratio of $|Li|/|$double bonds$|$ of 1.6 is satisfactory. There is a slow formation of a dark red precipitate (after 3 h) that is nearly complete in 24 h (for a double bond concentration of 0.17 mol l^{-1} with 2,11 diphenyl-1,11 dodecadiene). The precipitate is filtered and washed with hexane under vacuum to eliminate the soluble monofunctional derivatives.

It may be noted that dissolution of the precipitate in tetrahydrofuran gives a spectrum very similar to that of α-methylstyryl lithium carbanions with a λ_{max} at 340 nm.

INITIATION OF THE POLYMERIZATION OF DIENES

This dilithium initiator may be reacted with various monomers to give difunctional living polymers. We found that the initiator is quite stable for several months when kept in darkness at room temperature in the presence of an excess of BuLi.

In the case of dienes, seeds of low molecular weights were first prepared by adding an hexane solution of the diene to the insoluble initiator. For example, seeds of $\overline{M}_n$ ~3000 were obtained in about 15 min with butadiene and the initiator dissolved completely under stirring of the solution. Polymerizations carried out starting from these seeds have given polymers having the theoretical molecular weights and narrow distributions by g.p.c. The synthesis of homopolymers and of triblock copolymers will be described in a subsequent paper.

EXPERIMENTAL

α,ω Divinylidenyldiphenylalkanes

We describe the reactions for *n* equal to 8 but they can be easily applied to the preparation of other precursors of this series.

Sebacyldichloride. Was obtained quantitatively by reacting sebacic acid in benzene with thionyl chloride in excess[35].

1,10-diphenyl, 1,10 decadione. Finely divided $AlCl_3$ (145.5 g) and anhydrous benzene (250 ml) were poured into a three-necked flask equipped with a dropping funnel, a stirrer and a condenser. After the aluminium chloride had dissolved completely sebacyl dichloride (116 g) was added slowly while maintaining the temperature at ~45°C. At the end of the addition the stirring was continued for 6 h keeping the temperature at 50°C. (4 h at 50°C and 12 h at room temperature give the same result).

After cooling, hydrolysis was performed with a mixture of water and ice acidified with concentrated hydrochloric acid (20 ml). The grey white precipitate was collected on a filter and then washed several times with diethylether. It was then carefully dried and kept under vacuum before use. the 1,10 diphenyl-1,10 decadione was obtained with a yield of 80%.

Triphenylmethylphosphonium bromide. Triphenylphosphine (157.5 g) was dissolved in anhydrous benzene (200 ml) in a 1 litre flask equipped with a motor-driven paddle stirrer. After dissolution methylbromide (45.5 ml) was added progressively at −15°C from a graduated dropping-funnel equipped with a cooling system. The mixture was allowed to return to room temperature and was stirred for 72 h. A white precipitate was collected and washed with hot benzene (500 ml). The precipitate was dried in a vacuum oven at 100°C for 24 h and kept under vacuum in a desiccator containing P_2O_5. Triphenylmethylphosphonium bromide (m.p. 232.5°C) was obtained with a yield of 99%.

2,11 Diphenyl-1,11 dodecadiene. This compound may be prepared through a normal Wittig reaction or according to Corey[32] as follows.

0.1 Mol of HNa (in oil suspension) was washed with dry n-pentane of hexane under dry argon in a 500 ml flask containing a magnetic stirring bar covered with glass, a condenser, a dropping funnel, a gas inlet and closed with a rubber septum. The vessel was then evacuated and purged several times with dry argon. The reaction was conducted under argon.

Dry dimethylsulphoxide (50 ml) was introduced into the vessel and the mixture was heated at about 60°–80°C until the hydrogen bubbling ceased. The methylsulphuryl carbanion solution was then cooled down to −10°C and triphenylmethylphosphonium bromide (1 mol) dissolved in hot DMSO (100 ml) was added. The mixture was stirred for 20 min at room temperature and a solution of 1,10 diphenyl-1,10 decadione in tetrahydrofuran (THF) (120 ml for 47 g) was then cautiously added because of the high exothermicity of the reaction. After addition, the reagents were heated at 60°C for 5 h and kept for 12 h at room temperature. Water (100 ml) was then added and the mixture (aqueous and organic phases) was extracted 5 times with THF. Extraction with an aliphatic hydrocarbon gave a much lower yield (28%). THF was removed by evaporation and the residue (diene-dione-triphenylphosphineoxyde) was collected on a filter and washed with petroleum-ether (bp 30 ~ 75°C) which permits the elimination of the major part of φ_3PO. After concentration of the mother liquor the diene was purified twice through an alumina column and recrystallized in hexane or petroleum ether at about −30°C. The 2,11 diphenyl-1,11 dodecadiene was obtained with a yield of 40%.

The diene could be also prepared through a simple Wittig reaction in an apparatus similar to that used before. Triphenylmethylphosphoniumbromide (72 g) was added to an ether solution of n-butyllithium (0.2 mol). The solution was stirred for 4 h at room temperature. 0.1 Mol of 1.10 diphenyl-1,10 decadione was then added. The solution was heated under reflux for 24 h and the diene was recovered as described above (yield with aliphatic hydrocarbon extraction 15%).

The physical characteristics of 2,11-diphenyl-1,11 dodecadiene thus obtained are the following:

Melting point: ~30°C; ultra violet spectrum in n-hexane $= \lambda_{max}$ 237 nm, ε_{max} 2.15×10^4 mol^{-1} l^{-1} cm^{-1} (Beer's law has been verified between 10^{-2} and 10^{-6} mol l^{-1}).

N.m.r. spectrum:
- benzenic protons δ/TMS = 7.26 ppm
- vinylic protons = 5.16 and 4.96
- methylenic protons geminal to the double bonds $\delta = 2.40$
- methylenic protons of the chain $\delta = 1.21$

α,ω *Diisopropenyl diphenylalkanes*

The diisopropenyl diphenylalkanes may be prepared according to already published synthesis[33,36] with yields in agreement with those given in these papers. We will briefly describe the synthesis of α,ω-diisopropenyl diphenyl-1,2 ethane.

Bis-(acetoxy-4 phenyl)-1,2 ethane. This compound was syntheized according to Sloan *et al.*[36] by a Friedel–Crafts reaction of diphenyl-1,2 ethane on acetyl chloride in CS_2 with $AlCl_3$ as the catalyst. The product was recrystallized from dioxane after hydrolysis (m.p. 167°C; yield 65%).

Bis-|(hydroxy-2 propyl)-4 phenyl|-1,2 ethane. This diol was prepared through a Grignard reaction involving bis-(acetoxy-4 phenyl)-1,2 ethane and CH_3MgBr according to Markus[33]. The yield was 55% (m.p. 134°C).

Bis-isopropenyl-4 phenyl-1,2 ethane. The diol was dehydrated according to Markus[33] either by acetic anhydride in benzene or by a non catalytic process involving an azeotropic distillation. The diene was purified under vacuum under 10^{-3} mm Hg (yield 50%).

Preparation of the organolithium compound

All the operations were carried out under vacuum in all glass apparatus equipped with breakseals and u.v. cells as is usual in ionic polymerizations, but they may be carried out under inert gas flushing. The vessel used for the addition of BuLi on the precursor was also equipped with a sintered glass filter.

The 2,11-diphenyl-1,11 dodecadiene, dried in high vacuum was dissolved in purified hexane and for an ultimate purification was contacted with a sodium mirror for a few minutes. Ultra violet spectra before and after this operation did not show any reaction involving the precursor and sodium (but if the mixture remains in contact for too long the mirror may become yellow but the solution remain colourless). This purified solution was mixed with an excess of sec- or tert-butyl lithium and the organodilithium initiator precipitated after some time at room temperature and more quickly at 30–35°C. The supernatant solution had an orange red colour. The initiator was collected as a brownish-red compound which deposited in part on the walls of the vessel. After filtering the suspension through the sintered glass in order to eliminate the excess of butyllithium and the monofunctional species, the walls on the apparatus and the precipitate were washed with pure hexane. The efficiency of the washing may be checked by following u.v. spectra. Isoprene was then brought into contact with the purified initiator. The initially brownish red precipitate changed to yellow and then dissolved while isoprene reacted under stirring with the initiator to give a light coloured yellow solution. In the case of butadiene the precipitate dissolved to give a colourless solution of very stable telechelic polybutadienes.

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