New perfectly difunctional organolithium initiators for block copolymer synthesis:
3. Kinetics of addition of tert-butyllithium on 1,2-bis(isopropenyl-4 phenyl)ethane

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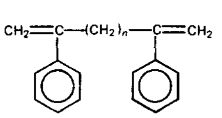
The precursor 1,2-bis(isopropenyl-4 phenyl)ethane may react in hexane with tert-butyllithium (tert-BuLi) to yield a difunctional initiator even if the reagents are in stoichiometric amounts. The kinetics of this reaction were investigated at various temperatures. Nuclear magnetic resonance and mass spectrometry show that the concentration of monoadduct remains small during the reaction and that the end product consists only of diadduct. When tert-BuLi is in excess, the two steps of addition can be treated as consecutive pseudo-first-order reactions. The much higher apparent rate constant for the addition of BuLi to the second double bond of the precursor may explain the low proportion of monoadduct.

(Keywords: dilithium initiator; synthesis; kinetics; anionic polymerization)

INTRODUCTION

Attempts to obtain efficient anionic difunctional initiators have led us in the last few years to the synthesis of new types of precursors. These compounds belong to two series, one with phenyl side groups and the other with the phenyl groups in the main chain:



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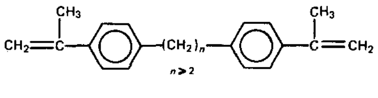

II

Their syntheses have been fully described in previous papers or patents[1-4]. In a hydrocarbon solvent, an excess of sec- or tert-BuLi is generally added to these precursors in order to give an insoluble dilithium adduct (initiator). The precipitate is filtered and washed with hexane to eliminate the soluble monofunctional derivatives. By addition of a monomer able to react with them, the dicarbanionic species are solubilized. With dienes such as butadiene or isoprene, they lead to seeds of low molecular weight which are quite stable.

Polymers and copolymers obtained from these seeds in order to verify their functionality, their molecular weight distribution and their stereoregularity have already been described[1-4].

In an overview and critical study of bifunctional initiators mentioned by various authors as good sources of dilithio living polymers, Bandermann *et al.*[5] found that compounds deriving from the first series (I) were the most efficient. They are free from oligomers and their rate of initiation of isoprene polymerization is the fastest. They lead to polymers having lower dispersity in spite of their low solubility in toluene, which was nevertheless considered as a drawback by the authors. However, stoichiometric conditions (difficult to achieve) are necessary to obtain more soluble dilithium initiators with precursors proposed by other authors.

The precursors belonging to the second series (II) are easier to prepare and less expensive. Those of the first series necessitate a Wittig reaction which generally gives low yields, and also phosphine oxide as a by-product.

Preliminary experiments have led to the conclusion that 1,2-bis(isopropenyl-4 phenyl)ethane (the first compound of the second series) reacted in stoichiometric conditions with tert-BuLi to give a difunctional initiator for the polymerization of butadiene. It seemed interesting to investigate the synthesis of the dilithium initiator further using this precursor. Our aims were (i) to check whether the two double bonds of this compound are equally reactive with BuLi and (ii) to determine more accurately the functionality of the adduct. The results of this study are described in this paper.

EXPERIMENTAL

The experiments were carried out according to the high-vacuum techniques usually used in our laboratory (all glass apparatus equipped with break-seals or Rotaflo^{R} devices).

Solvents

Hexane and toluene (Prolabo RP Normapur) were first fractionated under dry nitrogen at atmospheric pressure on sodium pieces. They were kept under vacuum on H_2Ca and then on sodium mirrors, then purified on active centres (polystyryllithium for toluene and n-BuLi for n-hexane). Before distribution in sealed tubes an ultimate purification was made on a sodium mirror.

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Monomer

Butadiene (Matheson) was kept under vacuum on anhydrous BaO for several days, then cryodistilled on several sodium mirrors and at least on n-BuLi. A new sodium mirror was made before distribution.

Tert-BuLi

(This was from Janssen Chimica.) After sublimation under high vacuum it was dissolved in anhydrous hexane and titrated by u.v. spectrophotometry[1-4].

Precursor

This was synthesized according to a procedure already described[1-4]. Nevertheless, the yield was noticeably enhanced compared to that already published and it may be possible to have a still better yield, a significant part of the diene being lost in the last step of the synthesis, i.e. during dehydration of the diol by azeotropic distillation.

Size exclusion chromatography

Analyses were performed on a Waters apparatus fitted with μ-Styragel columns (50, 100, 100, 500 Å) with 0.5 wt % solutions. Eluant was tetrahydrofuran (THF) at a $1.5\,\mathrm{ml\,min^{-1}}$ flow rate. Polymers obtained during the preliminary experiment were analysed with a 10^6, 10^5, 10^4, 10^3, 500, 100 Å set of columns. A differential refractometer and a u.v. detector (254 nm) were used.

Vapour-phase chromatography

Samples were analysed on a Girdel 32 apparatus fitted with a capillary column (Silicon 5, 0.37 mm diameter, 25 mm length) and a Nermag R 10-10 spectrometer as detector (70 eV). The injector was set at 250°C with a helium pressure of 1.7 bar. The column temperature was programmed from 100 to 270°C with a rate of $2^\circ\mathrm{C\,min^{-1}}$.

N.m.r. was made on some samples in $CDCl_3$ solution at room temperature using a Brüker ^1H 250 MHz apparatus.

RESULTS AND DISCUSSION

Preliminary experiment—polymerization of butadiene by an initiator prepared in stoichiometric conditions

A solution in n-hexane of 2 moles of tert-BuLi per mole of precursor P ($[P]=1\times10^{-3}\,\mathrm{mol\,l^{-1}}$) was kept for 6 days at 25°C under magnetic stirring. Afterwards, a small volume of butadiene was distilled in the medium and was polymerized for 24 h at 25°C. A small amount of solution was taken for g.p.c. analysis (peaks a and A in *Figure 1*) before adding another volume of monomer. The polymerization was terminated by a small addition of methanol after 60 h. The solution was directly analysed by g.p.c. (peaks b and B in *Figure 1*).

It is to be noticed that sensitivities used were not the same for the two g.p.c. analyses owing to the very small weight of product in the first sample. The small u.v. signal (a_1) corresponding to peak A is probably due to the absorption of the central aromatic rings of the low-molecular-weight polydiene which is detected with the high sensitivity used.

For the two samples, the refractive index (r.i.) signals corresponding to the polydienes are unimodal. However in both cases, a significant u.v. signal is observed at high elution volume ($\simeq$60 ml). This signal cannot be attributed to monofunctional initiator resulting from the addition of one tert-BuLi per mole of precursor since this would also have yielded macromolecules having molecular weights half those of the polymer resulting from difunctional initiation. This is also in agreement with the low polydispersity of the polymer formed. This signal might be that from unreacted precursor as this compound is eluted at the same elution volume (*Figure 3*). But initiation was not complete since a deposit of initiator remained tightly stuck on the reactor walls, especially at the meniscus level. We think that the main species responsible for the signal is the product resulting from hydrolysis of the insoluble diadduct.

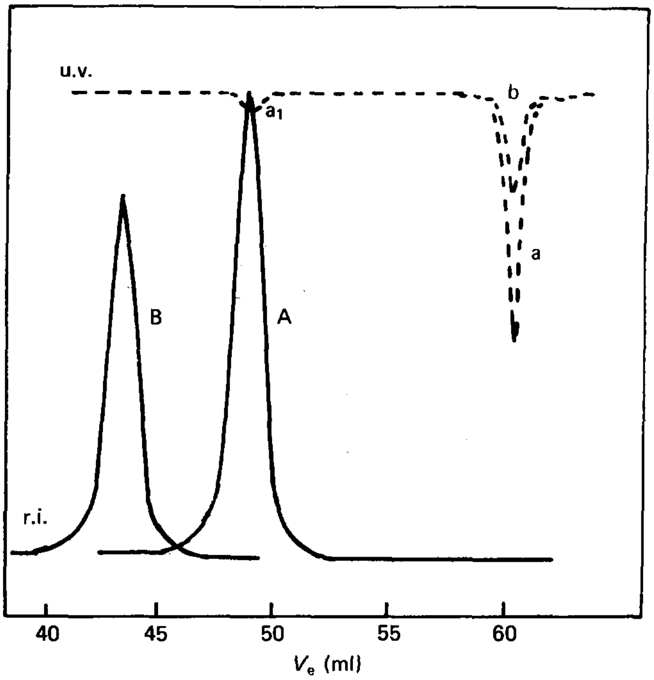

Figure 1 Preliminary experiment—g.p.c. analysis of polymers after a first (A,a,a_1) then a second (B,b) addition of butadiene

Owing to the presence of a single peak for each polymer we may conclude that initiation involved a single initiating species, likely bifunctional. It was then of interest to investigate the reaction of initiator synthesis further.

Kinetics of addition of tert-butyllithium on the precursor

Stoichiometric conditions. According to the experimental procedure we published before, the dilithium compounds deriving from our precursors were generally prepared with an excess of BuLi. However, owing to the preliminary experiment described above, it was interesting to investigate the reaction in stoichiometric conditions in order eventually to avoid filtration and washing of the precipitate before its solubilization owing to diene polymerization.

A first experiment was carried out at 70°C with a precursor concentration of $10^{-3}\,\mathrm{mol\,l^{-1}}$ in hexane solution. The reaction was followed by u.v. spectroscopy. The first stage of the reaction could be monitored by this method, but as the reaction proceeded, precipitation of the diadduct disturbed the u.v. titration. Nevertheless, after a long time of reaction (about 24 h) a new but weak band of absorption appeared at 500–510 nm. This absorption is probably due to secondary reactions as observed for spontaneous deactivation of living poly α-methyl *styryl* carbanions in solution or in bulk[6].

As the precipitation of the diadduct formed in hexane prevented direct measurement of the reaction yield, we titrated separately the concentration of soluble derivatives in the filtrated hexane solution and that of the remaining diadduct after dissolution in tetrahydrofuran. It is known that THF solutions of lithium derivatives are not very stable. Nevertheless, we were able to determine that the decomposition of active centres at 25°C obeys first-order kinetics with a constant of $6.7 \times 10^{-4}\,s^{-1}$. This value is in agreement with that found by Sigwalt *et al.*[7] in the case of poly(α-methylstyryllithium) ($2 \times 10^{-4}\,s^{-1}$ at 20°C). Using this result, an extrapolation of the concentration of diadduct derivative to initial time could be done. Despite these precautions, the values obtained with this procedure were lower than those of the nominal concentration of precursor introduced. We have no satisfactory explanation of this disagreement. Either the stability of the THF solution is too small to have an accurate measurement by extrapolation, or side reaction products disturbed the determination, or the value of the molar extinction coefficient ε taken equal to 12000[8] is questionable.

In order to reduce the secondary reaction that had occurred at 70°C, another set of experiments was carried out in hexane at 40°C with a higher precursor concentration ($3.8 \times 10^{-3}\,mol\,l^{-1}$). After mixing, the solution was immediately divided into several sampling tubes, one of them being fitted with a u.v. cell. The samples were put in a thermoregulated bath in the dark (that was not the case for the experiment described above). At given times, they were deactivated by adding a few drops of methanol and analysed after filtration to remove lithium methylate.

As in the previous case precipitation of the diadduct made the u.v. titration difficult. A general tendency may however be observed (see *Figure 2*). At the beginning of the reaction, the optical density at 330 nm first increased, then decreased continuously after about 12 h. This does not result from side reactions since in this experiment no absorption at 500–510 nm could be detected.

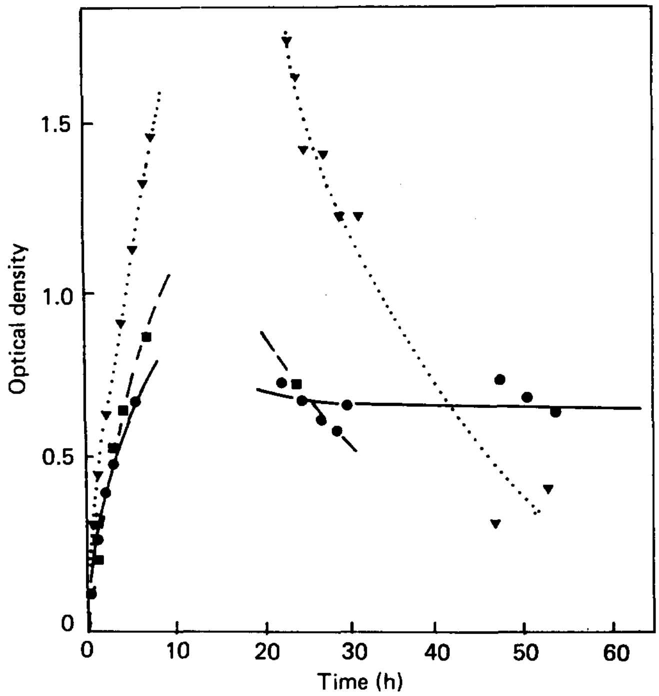

Figure 2 Plot of optical density ($\lambda_{max} = 330\,nm$) *versus* time for the reaction of tert-butyllithium with 1,2-bis(isopropenyl phenyl)ethane: stoichiometric conditions at 70°C (■) and 40°C (▼); with a 26-fold excess of tert-BuLi at 37°C (●)

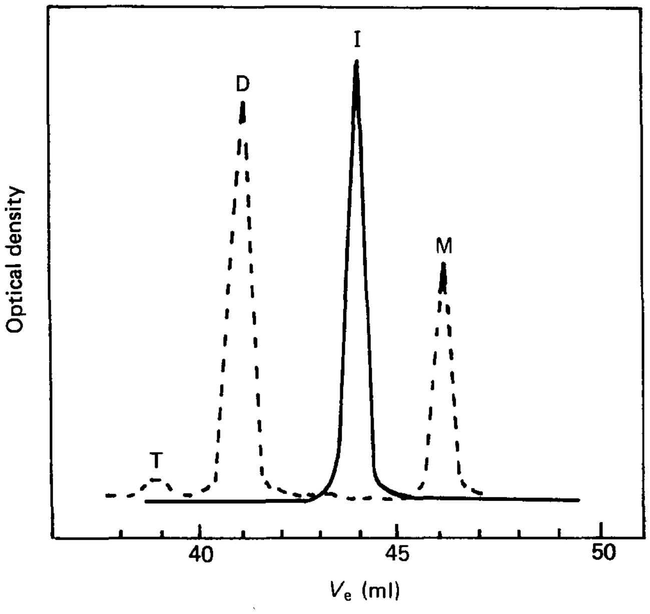

Figure 3 G.p.c. analysis of a mixture of precursor, mono- and diadduct (I) (———) and of a mixture of α-methyl-*p*-tert-butylstyrene (M) with its cationic dimers (D) and trimers (T) (-----)

As tert-BuLi was consumed, the amount of free tert-BuLi available for cross-associations with the diadduct derivatives decreased and the diadduct molecules tended to aggregate and to precipitate. At the end of the reaction the solution was nearly clear owing to the very low solubility of the initiator.

By g.p.c. in the THF eluant it was impossible to separate the reagents (precursor, mono- and diadduct) (see *Figure 3*). Analysis of a mixture of these three compounds yielded a single signal at the elution volume of the precursor. However this method showed that oligomerization of the precursor did not take place. In the same conditions of analysis we were able to separate α-methyl-*p*-tert-butylstyrene from its cationic dimers and trimers (as seen in *Figure 3*), the differences in molecular weight of which are smaller than between the precursor and its dimer.

The various samples were analysed by v.p.c. with a mass spectrometer as detector and sometimes by ^1H n.m.r. at 250 MHz (solvent $CDCl_3$). *Figure 4* gives the typical mass spectra of the three major compounds, i.e. precursor, mono- and diadduct. Other compounds were also detected but only to a minor extent ($\leqslant 0.1\%$) and their amount did not change during the reaction. Thus we can neglect them.

Some samples were analysed by ^1H n.m.r. A typical spectrum is given in *Figure 5*. This method allowed the determination of the content in precursor and in diadduct. Their fraction is given by the ratio of the integration of the signals e and f. The monoadduct was in a too small concentration to be detected.

The results are represented in *Figure 6*. It appears that the precursor and the diadduct are the main products in the mixture. Although always present, the concentration of monoadduct remains small. The aspect of the curves seems to be connected with an autoaccelerated process. We shall come back to this behaviour later.

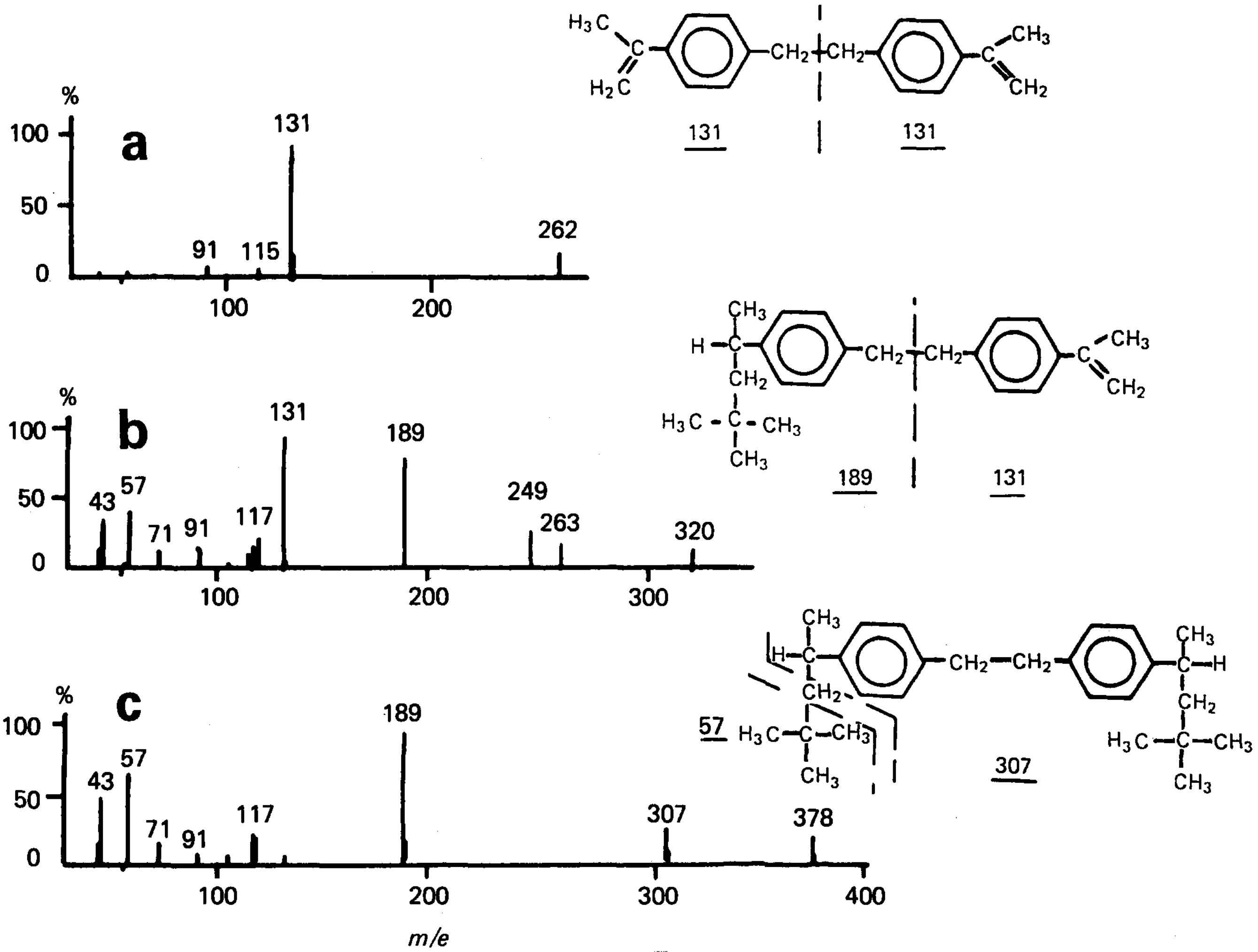

Figure 4 Mass spectra of (a) precursor, (b) monoadduct and (c) diadduct. Respective parent peaks: 262, 320 and 378

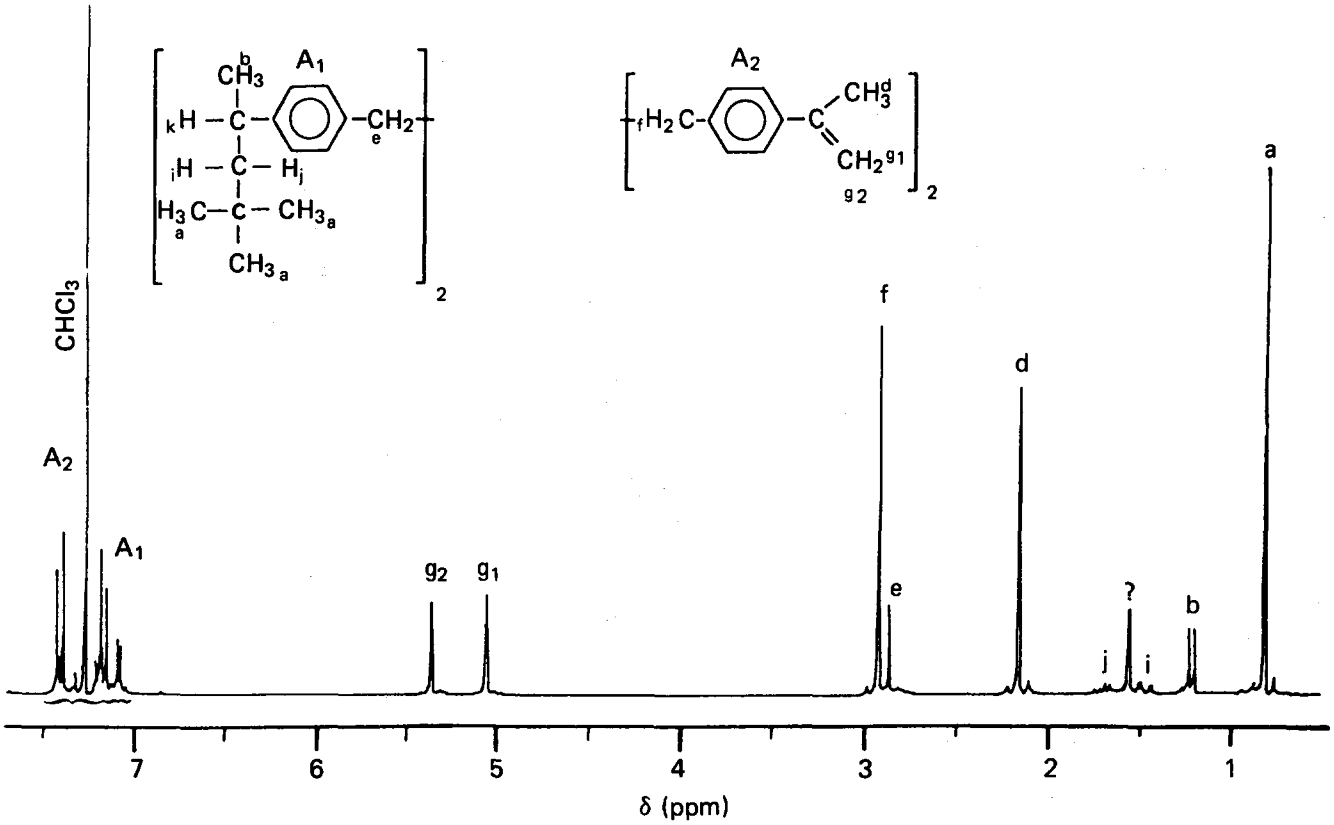

Figure 5 Proton n.m.r. spectrum (250 MHz) of a mixture of precursor, mono- and diadduct (sample corresponding to 22.5 h of reaction in stoichiometric conditions at 40°C)

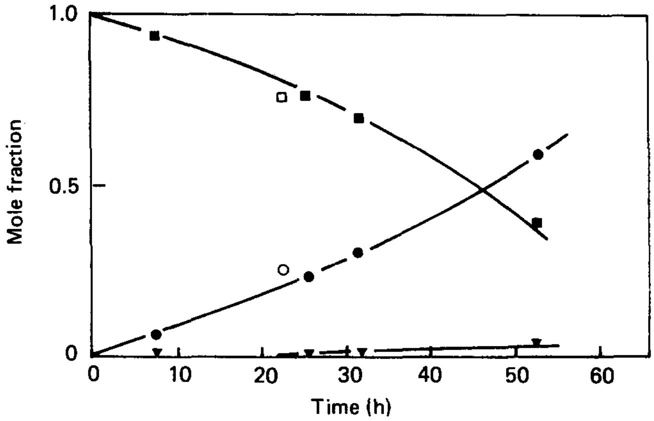

Figure 6 Kinetics of tert-BuLi addition to precursor in stoichiometric conditions at 40°C—composition *versus* time: precursor (■), diadduct (●) and monoadduct (▼); open symbols (□, ○) from n.m.r. analysis

Kinetics in the case of an excess of tert-BuLi. The experimental and analytical techniques were the same as described before. But in this case the tert-BuLi concentration was 26-fold that of precursor ($[P] \sim 4.6 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$) and the temperature was 37°C.

As in the previous cases, we observed the optical density at 330 nm (*Figure 2*). As already described the absorption first increased, but in this case it reached a more or less stable plateau after around 20 h of reaction. This behaviour is in agreement with what would be expected. Absorption increases as long as the initiator remains soluble (solubility is enhanced by cross-associations) and then becomes constant as soon as precipitation occurs. As we said before, u.v. spectra do not give an accurate measure owing to precipitation, which disturbs it and prevents a significant correlation of chromatographic and spectrometric analysis.

Owing to the experimental technique used we were unable to determine butane concentration, and only three compounds were found in measurable content. They are the precursor and the mono- and diadduct. The molar composition of the mixture as a function of time is given in *Figure 7*.

Interpretation of kinetic data. The tert-BuLi concentration is in large excess relative to other compounds and remains constant during the reaction. If $[P]$ is the precursor concentration at t time, $[P_0]$ its initial concentration, $[BP]$ and $[B_2P]$ the instantaneous concentrations of mono- and diadduct, the addition of tert-BuLi to the precursor can be treated as consecutive pseudo-first-order reactions:

$$P \xrightarrow{k_1} BP \xrightarrow{k_2} B_2P \qquad (1)$$

The differential equations characterizing this system can be written as:

$$-\frac{d[P]}{dt} = k_1[P] \qquad (2)$$

$$\frac{d[BP]}{dt} = k_1[P] - k_2[BP] \qquad (3)$$

$$\frac{d[B_2P]}{dt} = k_2[BP] \qquad (4)$$

Let us assume that $k_1 \neq k_2$. Integrations of the above differential equations lead to:

$$[P] = [P]_0 e^{-k_1 t} \qquad (5)$$

$$[BP] = [P]_0 \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \qquad (6)$$

$$[B_2P] = [P_0]\left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t}\right) \qquad (7)$$

Knowing $[P]$ and $[P_0]$ it is easy to determine k_1. The plot of $\ln([P]/[P_0])$ *versus* time is a straight line up to 70% of precursor consumption. Above this value, its concentration is too small to be measured with accuracy and therefore leads to a significant uncertainty in the logarithm (*Figure 8*).

The slope of this straight line gives the apparent rate constant k_1 of the precursor consumption. We found $k_1 = 0.028\,\mathrm{h^{-1}}$. However, k_2 is not obtained easily, and we have to use an iterative method. Putting the k_1 value determined into equation (7) we calculate $[B_2P]$ as a function of time for different k_2 values. By comparison with experimental values we found that k_2 was about 10 times the k_1 value. Taking $k_2 = 0.3\,\mathrm{h^{-1}}$, we have good agreement between theoretical curves and experimental values, within experimental errors as shown in *Figure 7*.

The determined rate constants are not absolute values. They include the tert-BuLi concentration taken as constant owing to its excess (26-fold) with respect to the precursor, without making any assumption on the 'active' form of BuLi (dissociation and initiation ability of

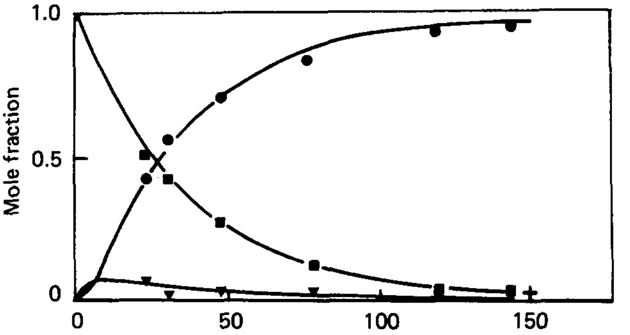

Figure 7 Kinetics of tert-BuLi (in 26-fold excess) addition to precursor at 37°C: theoretical curves (———) with $k_1 = 0.028\,\mathrm{h^{-1}}$ and $k_2 = 0.3\,\mathrm{h^{-1}}$; experimental values—precursor (■), diadduct (●) and monoadduct (▼)

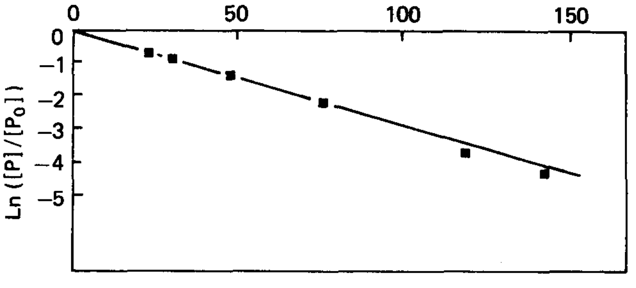

Figure 8 Determination of the apparent rate constant of tert-BuLi addition to the precursor first double bond at 37°C in hexane ($[P] = 4.6 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$, $[\text{tert-BuLi}] = 0.12\,\mathrm{mol\,l^{-1}}$)

organolithium aggregates are not yet fully understood or quantified). Nevertheless, even though they have no absolute meaning, the comparisons between the two rate constants are in our opinion valid.

The great dissimilarity found between these apparent rate constants may appear surprising. In fact, the two double bonds are non-conjugated and their reactivity should be equivalent towards BuLi. On account of the possibility of rotation around the CH_2–CH_2 bond the phenyl rings may take a boat conformation (angle of about 39° between the two benzene planes). Thus the two double bonds may become very close. Moreover, tert-BuLi is tetrameric in non-polar solvents[9]. A tetrahedral structure was proposed by Weiner *et al.*[10] in which the lithium and carbon atoms occupy the vertices of concentric interpenetrating tetrahedra. It may be understood that the second addition occurs more quickly than the first one owing to the conformation of the precursor and to the presence of tert-BuLi associated with the monoadduct.

As described above we observed that at long times of reaction the precipitation occurred more completely and the optical density was lower in the case of stoichiometric conditions. This is probably the result of cross-association between tert-BuLi and the adducts and therefore precipitation is more difficult to achieve when tert-BuLi is in excess.

Assuming that lithiated compounds are all tetrameric, we may have the following scheme with an excess of BuLi (B_4 being the tetramer of tert-BuLi):

$$B_4 + P \xrightarrow{k_1} PB,B_3 \xrightarrow{k_2} PB_2,B_2 \qquad (8)$$

This global reaction may be written without any assumption about the active form of BuLi (i.e. 'free' or associated). There is surely a cross-association between the monoadduct and BuLi remaining in solution and by analogy with tert-BuLi we assume it to be a tetrameric aggregate PB,B_3. Owing to this 'over-concentration' of tert-BuLi, the second double bond should react with it more quickly than the first one with B_4. The diadduct was also assumed to form cross-associations such as PB_2,B_2.

Since, in stoichiometric conditions, the reaction does not stop at 50% yield, this shows that PB_2, B_2 is able to react (either directly or after dissociation) with the precursor, giving PB_2:

$$PB_2,B_2 + P \xrightarrow{k_3} PB_2,B + PB \xrightarrow{k_4} 2PB_2 \qquad (9)$$

The kinetic curves of *Figure 6* show that the addition in stoichiometric conditions is autoaccelerated. This phenomenon may be understood if k_3 is greater than k_1, which means that PB_2,B_2 reacts more easily than B_4.

When tert-BuLi is in large excess, scheme (8) prevails in comparison with scheme (9), which is negligible as experimentally observed (*Figure 7*).

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