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Various types of aggregates in mono- or bifunctional polyisoprenyllithium in hydrocarbons

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The addition of *tert*-butyllithium on 1,2-bis(isopropenyl-4 phenyl)ethane in pure hexane leads to the quantitative synthesis of a dilithium compound as shown previously by analysis of the reactional mixture. Its characteristics of difunctional initiator for the synthesis of polydienes in pure hydrocarbon solvents was proved by indirect methods. In this study it is shown by mass spectrometry that difunctional oligopolyisoprene is solely obtained at the first stages of the initiation reaction. Viscosimetric measurements show that, for low degree of polymerization and low concentration in Li, cyclic aggregates are preferentially formed by intramolecular association. A ^{7}Li n.m.r. study in hexane of various mono- and difunctional organolithium compounds confirms their trend to associate in hydrocarbon solvents and, for α,ω-dilithiopolyisoprene, the influence of the chain length on the formation of aggregated species involving more than four lithium atoms. A change in the concentration in Li has little influence on the distribution of the various aggregates in the $4 \times 10^{-4} - 3 \times 10^{-3}$ mol l^{-1} Li concentration range. The addition of LiCl reduces the amount of the most associated species, while the presence of 15 vol% THF leads to their disappearance. Copyright © 1996 Elsevier Science Ltd.

(Keywords: organodilithium; polyisoprene; ^{7}Li n.m.r.)

INTRODUCTION

Anionic polymerization is considered as the best method to synthesize tailor-made polymers with well-defined structures. In this way, polydienes with low polydispersity index and mainly 1,4 structure are obtained through initiation by organolithium compounds in non-polar solvents. Both initiator or growing chains are aggregated and their structure as well as the polymerization kinetics are governed by the degree of association[1-4]. For propagation, for instance, the order with respect to the Li concentration is fractional suggesting the presence of inert aggregates in equilibrium with the active non-aggregated species.

In a previous paper[5], we reported that in pure *n*-hexane the kinetics of the polymerization of isoprene initiated by an organodilithium compound is governed not only by the Li concentration but also by the chain length. For low concentrations (i.e. $C < 5 \times 10^{-4}$ mol l^{-1}) an autoacceleration effect is observed up to a number-average degree of polymerization (DP) of about 500. The order in organolithium varies from 1 (low Li concentration, low DP) to 0.25 (low concentration, high DP). For high Li concentrations (i.e. $C > 5 \times 10^{-4}$ mol l^{-1}) the system behaves like a monofunctional one: the order in active centres is equal to 0.25 whatever the DP. This behaviour was explained by the existence of equilibria between linear and cyclic aggregates and their dissociated states. The equilibrium constants are related to the chain length and the different orders result from a change in the relative amount of each species. This hypothesis was partially supported by a preliminary study of ionic species by ^{7}Li n.m.r.[6]. Dilute solutions ($C < 5 \times 10^{-4}$ mol l^{-1}) of monofunctional organolithium compounds in *n*-hexane as models, i.e. *n*-BuLi, monofunctional polyisoprenyllithium and then α,ω-dilithiopolyisoprenes of various DP were examined. For DP$_n$ = 500 both mono- and dicarbanionic species give aggregates of the same type, whereas for DP$_n$ = 80 associated species involving more Li atoms have been observed for bifunctional living polymers. This phenomenon has been attributed to the fact that, for a bifunctional chain of low DP, intramolecular association leading to cyclic species may occur easily; moreover, intermolecular association involving several monocyclic and/or linear species could lead to the formation of larger aggregates. A computer simulation based on the kinetics and n.m.r. investigations has been developed with success. However, several uncertainties on the nature of the various ionic species still remained and it was of interest to study the effect of the Li concentration and to find more direct proof of the presence of cyclic species.

EXPERIMENTAL

The purification of reagents and polymerizations were carried out using high vacuum techniques (all-glass apparatus fitted with break-seals).

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Reagents were purified according to procedures described previously[7,8]: solvents and monomer were dried on CaH_2 or BaO then on sodium mirrors after fractionated distillation.

Tert-BuLi (Aldrich) was purified by sublimation before use and dissolved in pure hexane. It was used for the synthesis of monofunctional poly(isoprenyllithium) and to prepare the α,ω-dilithiopolyisoprenes through addition on the 1,2-bis(isopropenyl-4-phenyl)-ethane precursor[7].

Concentration of active centres was measured using ultraviolet (u.v.) absorption[7].

Polymers were analysed by size exclusion chromatography with a 10^6, 10^5, 10^4, 500 and 100 Å set of μ-styragel columns and tetrahydrofuran (THF) as eluent (flow rate $1\,\mathrm{ml\,min^{-1}}$). The molecular-weight calibration curve was obtained using polyisoprene standards. Molar masses were measured using osmometry (Mechrolab 500 or Knauer Dampfdruck Osmometer) with respectively toluene and methylene chloride as solvents. The difunctional polyisoprene of low molecular weight ($DP_n \sim 3$) was analysed by Matrix-Assisted Laser Desorption/Ionization Time-of-flight (MALDI-TOF) mass spectrometry using 2,5-dihydroxybenzoic acid as matrix. The solvent was THF and the accelerating voltage was 20 kV.

The ^{7}Li n.m.r. study was performed on samples sealed under high vacuum in n.m.r. tubes after addition of 10 vol% of C_6D_6 to the hexane solution for the internal lock. LiCl in D_2O was used as external reference and chemical shifts are referred to this standard. More details are given in a previous paper[6].

RESULTS AND DISCUSSION

Mass spectrometry (MALDI-TOF) of the difunctional polyisoprene of $DP_n = 3$

Preparing a perfectly difunctional organolithium initiator through the addition of a monofunctional lithium compound on a diethylenic compound (precursor) is difficult to achieve. During the addition of *tert*-BuLi on 1,2-bis(isopropenyl-4 phenyl)ethane in hexane the amount of monoadduct was always very small[9], the reactivity of the second double bond being enhanced by the proximity of the lithium compounds and their ability to associate. Moreover, the good agreement between theoretical and experimental molar masses, the unimodal distribution and the good mechanical properties of polystyrene-*block*-polybutadiene-*block*-polystyrene[8] lead to the conclusion that the resulting initiator is perfectly difunctional. Nevertheless, no information on its behaviour in the first stage of the polymerization of dienes were available. So a sample having a DP_n of about 3 was examined by MALDI-TOF mass spectrometry. As a result only signals corresponding to DP = 2, 3, 4, 5, 6 and 7 ionized by Na^+ or K^+ are detected as shown in *Figure 1*. Particularly, the main peak at $m \approx 555$ (corresponding to the molecular weight of two isoprene units added to the initiator molecule) shows the predominance of the dimeric species. But, the main point is the absence of peak corresponding to 'DP = 1' (addition of only one isoprene monomer unit). As the reaction medium did not exhibit any u.v. absorption showing the presence of α-methylstyryllithium, it may be assumed that both carbanionic functions of the dilithium initiator add preferentially isoprene, in good agreement with the higher reactivity of α-methylstyryl carbanions compared to isoprenyl ones. So oligomers seem really to be α,ω-dilithiopolyisoprenes.

Viscosimetric study of α,ω-dilithiopolyisoprene

As described earlier the kinetics of the polymerization of isoprene initiated by the dilithium initiator in hexane are governed by the Li concentration and the length of the chains[5]. For DP_n up to 500 and a concentration lower than $5 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$, intramolecular associations are favoured as corroborated by a computer simulation involving various equilibria between inter- and intramolecular aggregates. So it was of interest to study the

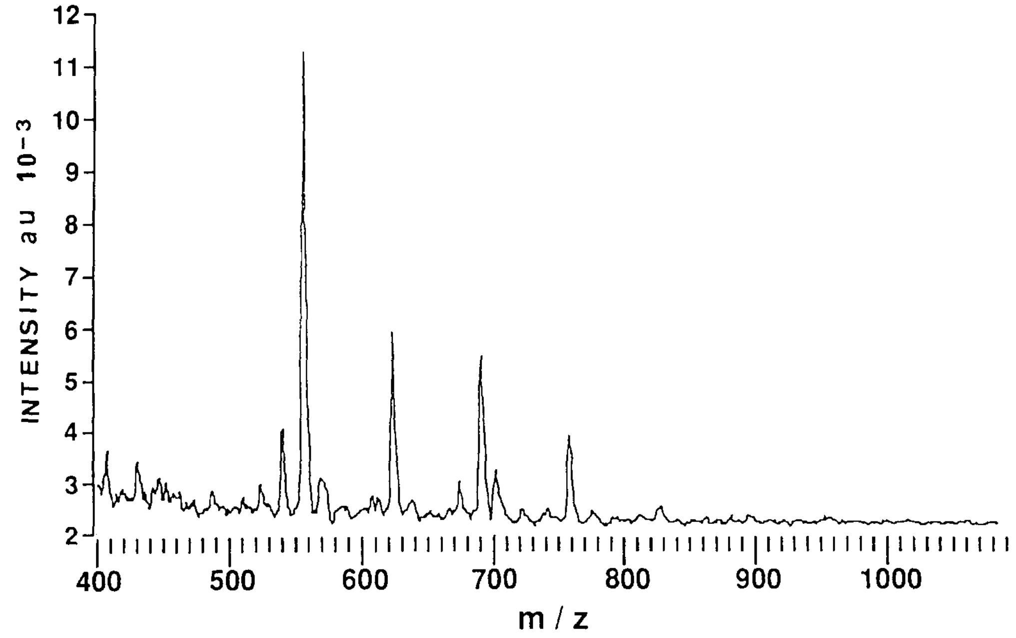

Figure 1 MALDI-TOF mass spectrum of a difunctional polyisoprene of $DP_n = 3$

Table 1 Flow times (in s) of the bifunctional living and deactivated polyisoprene solutions and of pure solvent at various temperatures

	$T = +18.5°C$	$T = +1.5°C$	$T = -2.85°C$
Living polymer	100.0	117.0	162.6
Deactivated polymer	101.3	121.9	169.1
Pure solvent	97.2	112.1	155.8

viscosity of a low molar mass α,ω-dilithiopolyisoprene ($DP_n = 180$) at a concentration lower than 5×10^{-4} mol l^{-1} (i.e. 3.6×10^{-4} mol l^{-1}). This was performed under high vacuum by measuring and comparing the flow time of the bifunctional living polymer, of the corresponding deactivated polymer and of the solvent at three temperatures, i.e. +18.5, +1.5 and −28.5°C. These results are reported in *Table 1*.

Due to experimental conditions, the differences of flow times for given solutions and temperature are small but for each value reported in *Table 1*, several measurements showing a good accuracy (±0.2 s) were made.

For monofunctional polymers the flow time for a living polymer is higher than that of the same deactivated solution. This behaviour is well explained by the existence of intermolecular association between active centres giving, e.g. dimer or tetramer, the hydrodynamic volume of which is greater than that of non-associated species. Owing to this behaviour, some authors tried to determine the degree of association of the chains taking into account that the flow time is related to the viscosity and therefore to the molecular weight[4,10]. Nevertheless, such a relation is valid only for dimers (and not for branched polymers) and in a restricted domain of molar masses. This explains the controversial interpretations based on such a method.

Surprisingly, the present study shows that at each temperature the flow time for the bifunctional living polymer is lower than that of the same deactivated polymer solution (we observed also that flow times for the living polymers are less sensitive to temperature than for dead polymers and variations are close to that of pure solvent). This may be the result of intramolecular associations giving cyclic species with an hydrodynamic volume lower than that of the terminated chains. Indeed, theoretical studies[11–15] have demonstrated that the gyration radius of a cyclic polymer is lower than that

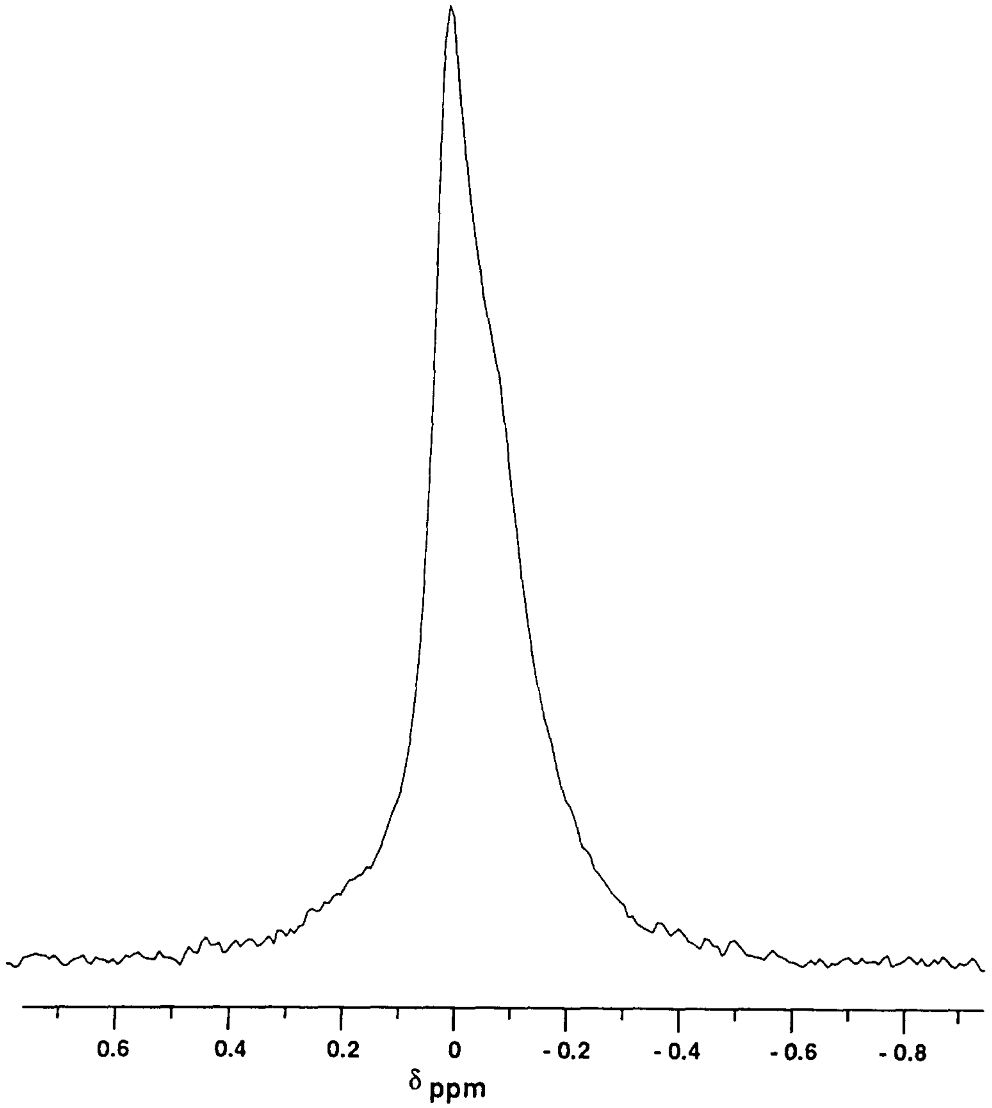

Figure 2 ^7Li n.m.r. spectrum of a monofunctional polyisoprenyllithium ($DP_n = 260$) in a mixture of hexane and C_6D_6 (90/10 v/v) at 7°C. Li concentration = 6×10^{-4} mol l^{-1}

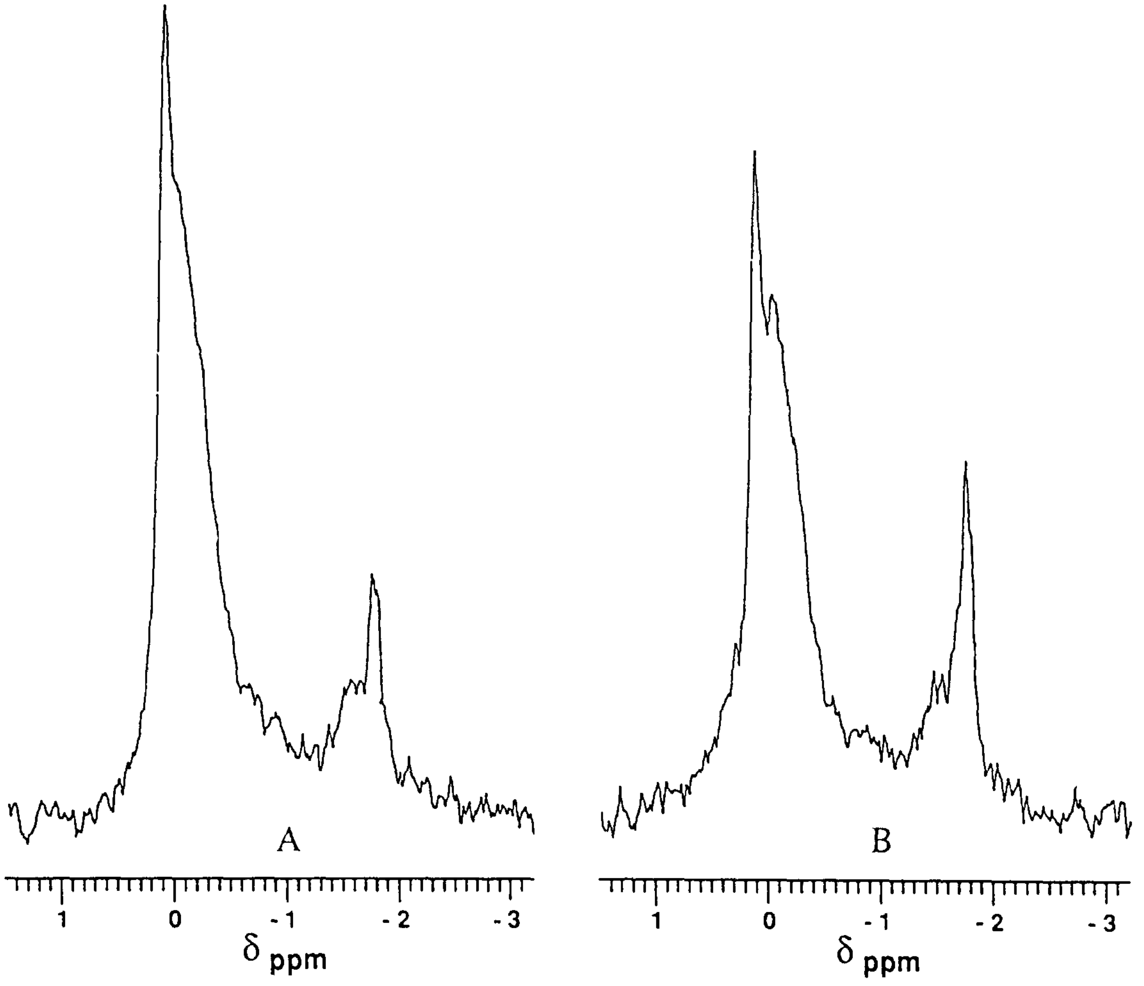

Figure 3 ^{7}Li n.m.r. spectra of a α,ω-dilithiopolyisoprene (DP$_n$ = 180) in solution in a mixture of hexane and C_6D_6 (90/10 v/v) at 7°C and two Li concentrations: (A) 7×10^{-4} mol l^{-1}; (B) 2.5×10^{-4} mol l^{-1}

of a linear polymer having the same molar mass and as a consequence the intrinsic viscosity of the cyclic polymer is lower than that of the linear equivalent. In the present study, however, flow times were measured at a single concentration and the results could not be extrapolated to give the intrinsic viscosity, but they are in good agreement with the formation of cyclic species resulting from intramolecular association.

^{7}Li n.m.r. study of mono- and bifunctional polyisoprenyllithium

Li n.m.r. is an interesting tool to study organolithium compounds. Although ^{6}Li n.m.r. is very accurate (hyperfine structure resolution), ^{7}Li n.m.r. is more often used since it is simpler to realize. A resonance signal corresponds to species having a given association degree, the most associated ones appearing at the lowest chemical shift. A decrease in temperature leads to a broadening of the linewidth linked to a decrease of the rate of exchange of lithium atoms. Moreover the dynamic behaviour of alkyllithium compounds is dependent of the inter- and intra aggregates exchange rate.

A previous paper[6] showed that α,ω-dilithiopolyisoprenes of high DP$_n$ exhibited ^{7}Li n.m.r. spectra similar to those of monofunctional ones even for low concentration. For low DP (< 500) and low concentrations ($C < 5 \times 10^{-4}$ mol l^{-1}) new resonances appear upfield, showing the existence of more associated species. In order to study this behaviour in more detail, the effect of the Li concentration and of the chain length for mono- and bifunctional polyisoprenes were reexamined.

Monofunctional polyisoprenyllithium

A monofunctional polyisoprenyllithium of DP$_n$ = 8 was previously studied[6] at a relatively 'high' Li concentration ($C = 10^{-3}$ mol l^{-1}) at −20 and −50°C. The spectrum exhibited two main resonances at 0.02 and −0.10 ppm. These two signals were assigned to dimeric and tetrameric aggregates respectively.

To study the effects of the chain length and the Li concentration, a monolithium polyisoprene of DP$_n$ = 260 at 6×10^{-4} mol l^{-1} was examined. At 7°C, the spectrum shows a single broad peak at 0.02 ppm (*Figure 2*). This result seems to indicate that the aggregation state is slightly affected by the concentration of ionic species and/or by the chain length up to DP$_n$ = 500.

Bywater *et al.*[16–18] have proposed that monofunctional polyisoprenyllithium is associated as tetramer in equilibrium with dimers, the latter becoming predominant when the concentration decreases. The same authors have also shown that the dissociation constant increases by a factor 50 when the molar mass increases from 500 to 12 500 in cyclohexane.

The sample analysed in this work (*Figure 2*) has a higher molar mass and its concentration is lower than

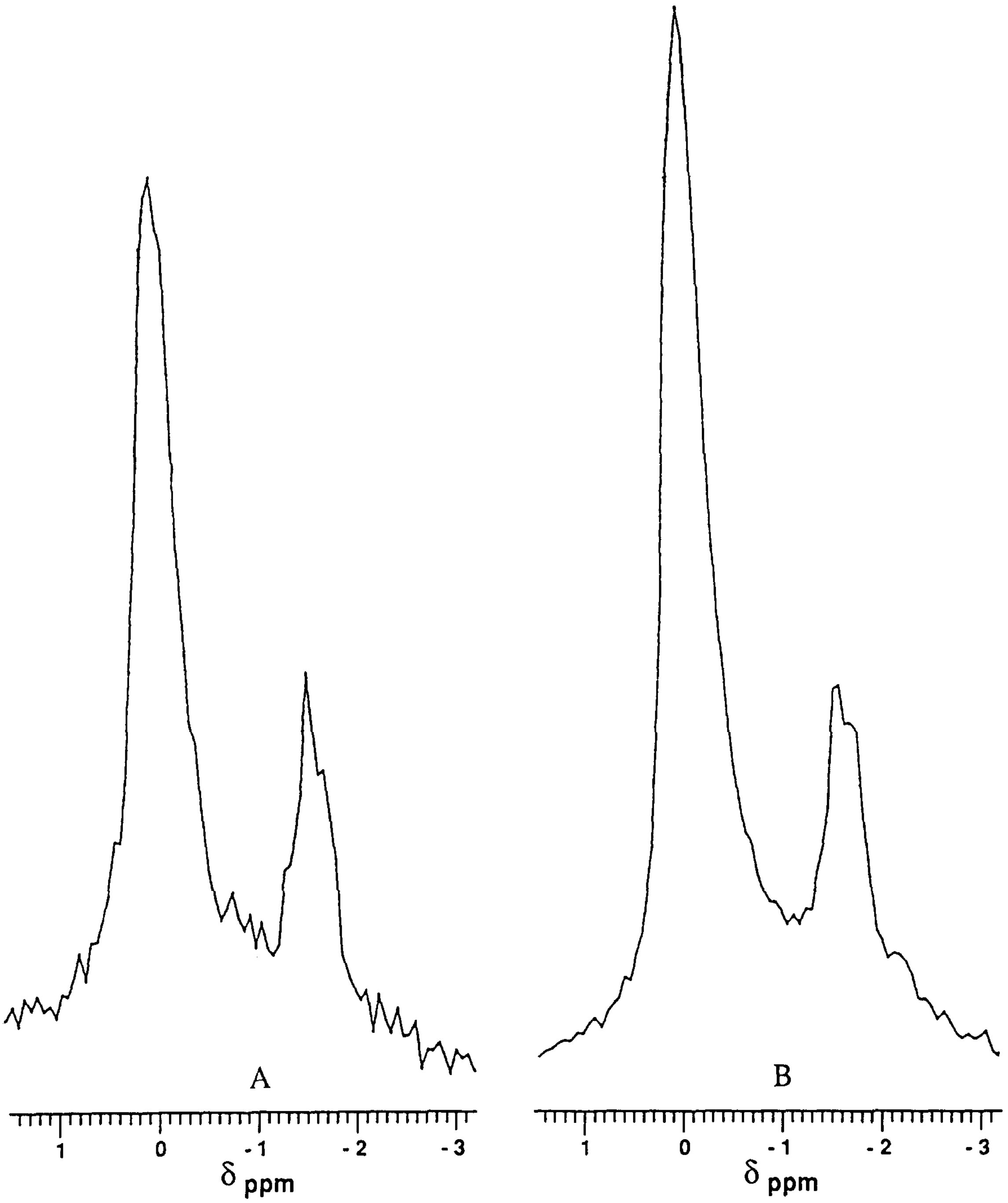

Figure 4 ^{7}Li n.m.r. spectra of a α,ω-dilithiopolyisoprene ($DP_n = 3$) in solution in a mixture of hexane and C_6D_6 (90/10 v/v) at 7°C and two Li concentrations: (A) 4×10^{-4} mol l^{-1}; (B) 3.2×10^{-3} mol l^{-1}

that of the sample previously described[6]. As a consequence, following Bywater[16], the proportion of tetrameric species (shoulder around −0.10 ppm) with respect to dimers should be lower. A tentative deconvolution of the two spectra is in favour of such a conclusion, but the observed effects are not significant enough owing to differences in the recording of the two spectra (see ref. 6).

α, ω-Dilithiopolyisoprene

Two samples having DP_n equal to 80 and 500 respectively at a concentration of 5×10^{-4} mol l^{-1} were previously analysed[6]. For both cases a resonance of 0.03 ppm similar to that of a monofunctional polymer was observed, but also for the lowest DP_n new resonances at −1.64, −1.85 and −1.92 ppm appeared resulting from more associated species. The peak at −1.92 ppm and the resonances at −1.64 and −1.85 ppm were tentatively assigned respectively to cyclic aggregates (C_4) involving four monocyclic species and to mixed association between linear (L) and cyclic aggregates.

In the present paper, the results obtained for two α,ω-dilithiopolyisoprenes having different DP_n from those analysed previously are compared, and the influence of the Li concentration on the various aggregate distribution is examined.

For a concentration of 7×10^{-4} mol l^{-1} the spectrum recorded at 7°C of the sample having $DP_n = 180$ (S_1) is similar to that of the sample of $DP_n = 80$. Two main groups of resonances are observed (*Figure 3*, Spectrum A). The first display a main peak at 0.03 ppm and three resonances at −0.1, −0.23 and −0.3 ppm. The second group shows the presence of more associated species at

-1.64, -1.74 and -1.90 ppm. Slight differences with the previously published spectrum either for chemical shifts or for relative intensities of the various peaks are nevertheless observed.

It is not possible to assign each signal to a given ionic species because of the presence of cyclic and linear aggregates. Indeed, assuming that a given peak corresponds to a definite environment for the lithium atoms, this peak may result from the existence of several kinds of aggregates. For instance, the resonance at 0.03 ppm similar to that of a monofunctional living polymer may be assigned to aggregates involving two atoms of lithium. Due to intra- and intermolecular associations, two aggregates are to be considered: the monocycle and the linear dimer.

The same polymer was analysed at a lower Li concentration, i.e. 2.5×10^{-4} mol l^{-1} (*Figure 3*, Spectrum B); the shape of the spectrum is not quite different from the one obtained for 7×10^{-4} mol l^{-1}. An approximate integration of the area of the two main groups shows that the proportion of signals appearing upfield remains close to 20% for both concentrations. This result is in accordance with the model previously published[6] which shows that the effect of the Li concentration might be significantly observable only in a particular and sufficiently large domain of concentration.

An oligomer of very low molar mass (S_2) ($DP_n = 3$) was also analysed at two Li concentrations of 3.2×10^{-3} mol l^{-1} and 4×10^{-4} mol l^{-1}. The spectra are reported in *Figure 4*. Two main groups of resonances are visible as for $DP_n = 180$. The chemical shift of the main peaks are respectively 0.01 and -1.59 ppm. This last value is higher than that of sample S_1 (e.g. $\delta = -1.84$ ppm), showing that species of a high degree of association are in a smaller amount with respect to sample S_1. It may be assumed that the polymer chains are too short to undergo intramolecular association. The concentration seems to have little effect on the distribution of the associated ionic species. The intensity of the peak at -1.75 ppm seems to increase slightly vs. the intensity at -1.59 ppm with the concentration. Nevertheless the ratio of their total area does not change (25% for the upfield resonances).

α,ω-Dilithiopolyisoprene in the presence of LiCl

When cyclic polymers are synthesized by adding a dichlorosilane to a solution of α,ω-dilithiopolyisoprene, LiCl is formed as a by-product. It was of interest to study the behaviour of such a mixture by ^{7}Li n.m.r. Therefore, about 30 mol% of dimethyldichlorosilane was added to a solution of difunctional seeds ($DP_n = 200$) and the mixture (Li concentration $= 5 \times 10^{-4}$ mo l^{-1}) was analysed by ^{7}Li n.m.r. The spectrum is reported in *Figure 5*. Two main peaks at 0.03 and -1.63 ppm are observed, with a broadening of the main signal at about -0.20 ppm. By comparison with the spectrum of the S_1 seeds ($DP_n = 180$), the main resonance at 0.03 ppm remains visible but the peaks between -1.7 and -1.9 ppm have vanished. Therefore, addition of LiCl leads to a decrease of the fraction of the highest degree of association and it may be assumed that the peak at -1.63 ppm corresponds to mixed aggregates between LiCl and living polymer chains.

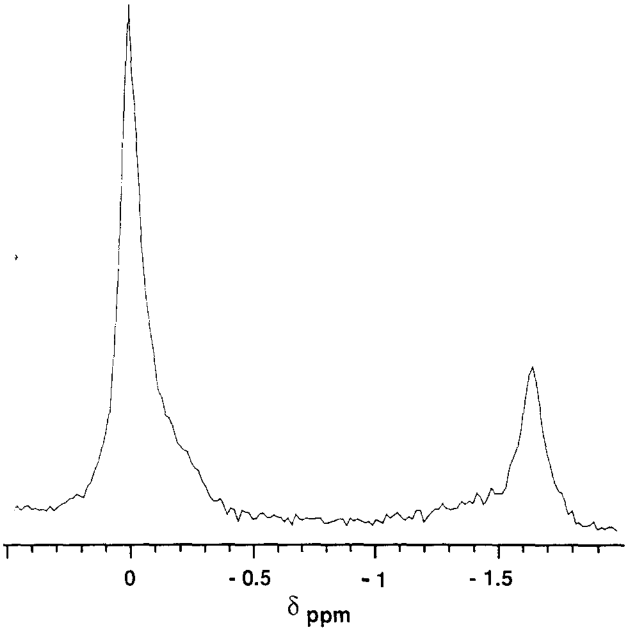

Figure 5 ^{7}Li n.m.r. spectrum of a α,ω-dilithiopolyisoprene ($DP_n = 200$) in solution in a mixture of hexane and C_6D_6 (90/10 v/v) at 7°C in the presence of LiCl. Li concentration $= 5 \times 10^{-4}$ mol l^{-1}

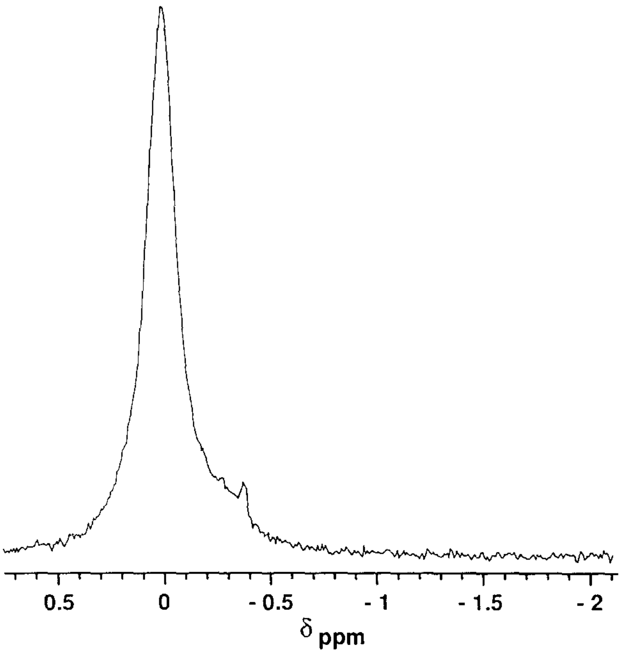

Figure 6 ^{7}Li n.m.r. spectrum of a α,ω-dilithiopolyisoprene ($DP_n = 200$) in solution in a mixture of hexane, C_6D_6 and THF (75/10/15 v/v) at -50°C. Li concentration $= 3.8 \times 10^{-4}$ mol l^{-1}

α,ω-Dilithiopolyisoprene in the presence of THF

Cyclization of α,ω-dilithiopolyisoprene by addition of 1,2-bis(isopropenyl-4-phenyl)ethane requires the addition of THF[19]. Its effect on the ^{7}Li n.m.r. spectrum of a solution of difunctional seeds ($DP_n = 200$) in hexane was examined. THF (15 vol%) and C_6D_6 (10 vol%) were successively added by cryo-distillation to the solution of living polymer cooled at -50°C. The concentration in active centres was 3.8×10^{-4} mol l^{-1}. The yellow solution was kept at this temperature after sealing in order to avoid deactivation of isoprenyl carbanions which are not very stable in the presence of polar solvents at room temperature[20]. The spectrum recorded at −50°C is reported in *Figure 6*. A main peak at 0.02 ppm and a smaller signal at −0.37 ppm are observed. So the addition of 15 vol% of THF does not affect the chemical shift of the main peak but suppresses the more associated species since peaks at −1.6 and −1.9 ppm have disappeared. These observations are partially supported by other authors[4,21], but do not agree if ^{7}Li n.m.r. may be regarded as sufficiently sensitive, with a dissociation of all aggregated species into THF-solvated species, as proposed by Bywater *et al.*[21] in the case of polybutadienyllithium in THF–hydrocarbon mixtures.

CONCLUSIONS

The synthesis of a perfect organodilithium compound through the addition of a monolithium on a diethylenic compound is difficult to achieve. We previously showed that during addition of *tert*-BuLi on 1,2-bis(isopropenyl-4-phenyl)ethane in pure hexane the amount of the monoadduct is always very small. In this study we have shown by mass spectrometry (MALDI-TOF) that only α,ω-dilithiopolyisoprenes of very low DP are really obtained in the first stage of the initiation of isoprene polymerization in pure hexane.

Although measurements were made at a single concentration, the viscosimetric study showed that for low DP_n and low concentration in lithium, α,ω-dilithiopolyisoprene formed preferentially cyclic aggregates by intramolecular association. This observation corroborates our previous results.

The study by ^{7}Li n.m.r. in hexane of various mono- and difunctional organolithium compounds has allowed us to confirm their trend to associate in hydrocarbon solvents. In the case of difunctional polymer, due to the presence of two Li atoms on the same chain, cyclic aggregates could be formed which are also able to associate with linear chains.

For α,ω-dilithiopolyisoprene we confirm our previous results on the influence of the chain length of the living polymer on the ^{7}Li n.m.r. spectra. For low DP_n, besides the main resonance at about 0 ppm, characteristic of associations involving four lithium atoms, signals appear upfield (−1.6 to −1.9 ppm). This may be explained by the existence of aggregated species involving more than four lithium atoms.

A change in the concentration in active centres has no significant influence on the distribution of the various aggregates, at least in the range $4 \times 10^{-4} - 3 \times 10^{-3}$ mol l^{-1}.

The addition of THF (15 vol%) to a solution of α,ω-dilithiopolyisoprene at low temperature leads to the disaggregation of the more associated species.

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