initial weight loss occurred at about this temperature. The data of the thermal behavior are summarized in Table IV.

In summary, we have shown that poly(aliphatic sulfides) with high molecular weights are readily prepared by the polycondensation of sodium sulfide with dibromoalkanes in the presence of quaternary ammonium salts such as CTMAC or CTMAB and phosphonium salts such as CTBPB. Since this preparative method is simple and gives quantitatively polysulfides of high molecular weight, it is generally superior to conventional methods for the synthesis of poly(aliphatic sulfides).

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Anionic Polymerization of Isoprene by Oligoisoprenyllithium/Tertiary Polyamine Complexes in Cyclohexane. 2. Proton Magnetic Resonance and Ultraviolet Spectroscopy of Propagating Living Species

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ABSTRACT: The nature of oligoisoprenyllithium complexed with TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) or PMDT (pentamethyldiethylenetriamine) is investigated by proton magnetic resonance and ultraviolet spectroscopy as a function of r = [tertiary polyamine]/[living ends]. ^{1}H NMR shows an upfield shift of both triplets corresponding to the methinic proton in the living unit and a simultaneous trans/cis isomerization of the living ends. The ultraviolet spectra confirm the NMR results and provide information concerning the association of the living species.

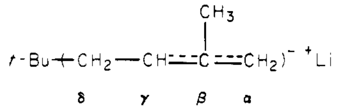
Introduction

The kinetic study of the anionic polymerization of isoprene by the complexes of oligoisoprenyllithium with tertiary polyamines in cyclohexane has been intensively developed in a previous paper.[1] *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) and pentamethyldiethylenetriamine (PMDT) were used as complexing agents. In the present paper the nature of the propagating living species is investigated by proton magnetic resonance and ultraviolet spectroscopy.

The structure[2-12] and the stability[3,13-18] of the propagating living species in the anionic polymerization of dienes (butadiene and isoprene) without tertiary polyamines have been studied in great detail. The purpose of this paper was dictated by the discrepancy existing concerning the mechanism of polymerization in the presence of such complexing agents.[1]

Results

1. Proton Magnetic Resonance of Oligoisoprenyllithium Complexed with TMEDA. An oligoisoprenyllithium of polymerization degree 1.2 is synthesized under vacuum by reaction of *tert*-butyllithium with isoprene in benzene. The living species in solution in C_6D_6 is characterized at room temperature by ^{1}H NMR (100 MHz); its behavior will be roughly the same in cyclohexane. The living oligomer is generally described by the following delocalized structure:[2-12]



$$t\text{-Bu}\!\left(\underset{\delta}{CH_2}-\underset{\gamma}{CH}\,{\overset{\cdots}{=}}\,\underset{\beta}{\overset{\overset{CH_3}{|}}{C}}\,{\overset{\cdots}{=}}\,\underset{\alpha}{CH_2}\right)^{-}\,{}^{+}Li$$

The low-field area is most informative. In the absence of TMEDA (r = [TMEDA]/[living ends] = 0) we observe triplets at 4.60 and 4.85 ppm from Me_4Si caused by the γ proton in the cis and the trans forms, respectively, of the living unit (Figure 1). The trans/cis ratio is about 2:1.

Addition of TMEDA to oligoisoprenyllithium induces important changes (Figures 1 and 2): (i) the two triplets shift upfield as r is increased from 0 to 1 and (ii) simultaneously a trans/cis isomerization occurs. Only the cis triplet is observed for r = 0.5; thus the living complexed species has a cis-4,1 configuration.

These results provide information concerning the nature of the propagating species in the polymerization of isoprene by the oligoisoprenyllithium/TMEDA complex in nonpolar solvents. Indeed, the upfield shift demonstrates an increase of electron density on the γ carbon, as shown in polar solvents.[9,11] A parallel increase of 4,3 and 1,2 links must be observed in the polymer; isoprene polymerization in nonpolar solvents and in the absence of TMEDA leads to a predominantly *cis*-4,1-polyisoprene, although the living species has mainly a trans structure.[19]

On the other hand, a complete isomerization for r = 0.5 suggests complexation of all living ends, the oligo-

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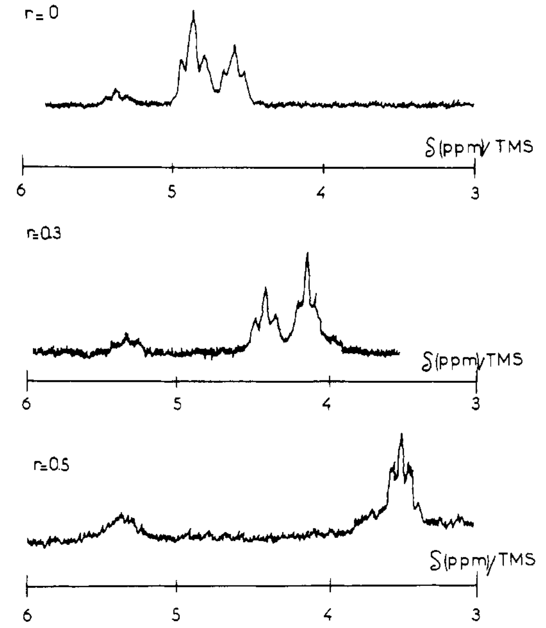


Figure 1. ^{1}H NMR (100 MHz) spectra of oligoisoprenyllithium in deuterated benzene: evolution of the spectrum as a function of r (polymerization degree 1.2, T = 20 °C).

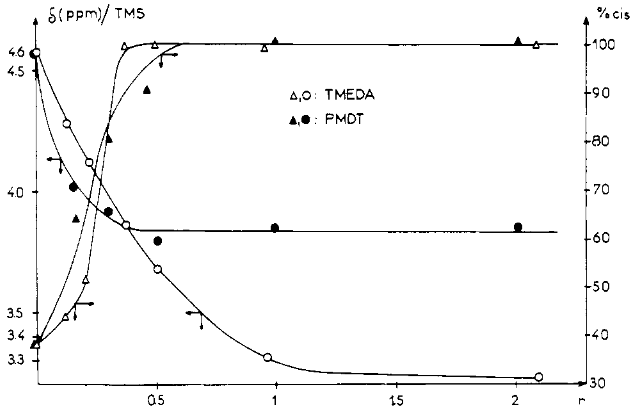
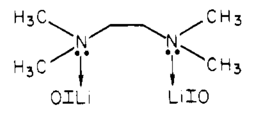


Figure 2. Upfield shift of the γ proton in the cis living unit and evolution of the cis content in the living unit as a function of r.

isoprenyllithium having then the dimeric structure $(OILi)_2 \cdot$TMEDA (where OILi stands for oligoisoprenyllithium).

The structure of such a complex should be



Each free electron pair from the nitrogen atom "complexes" one molecule of living species. However, the maximum shift is reached for r = 1, suggesting the presence of a species like (OILi·TMEDA).

2. Proton Magnetic Resonance of Oligoisoprenyllithium Complexed with PMDT. The ^{1}H NMR study of oligoisoprenyllithium complexed with PMDT shows the two important effects observed in the case of TMEDA (Figure 2): (i) an upfield shift of the two triplets corresponding to the γ proton and (ii) a trans/cis isomerization.

However, in the case of PMDT a slightly different behavior is observed. It seems that for r = [PMDT]/[living ends] $\geq$ 0.5 no observable shift of the cis triplet is observed. On the other hand, a full isomerization at r = 0.5 suggests the existence of the complexed active species $(OILi)_2 \cdot$PMDT.

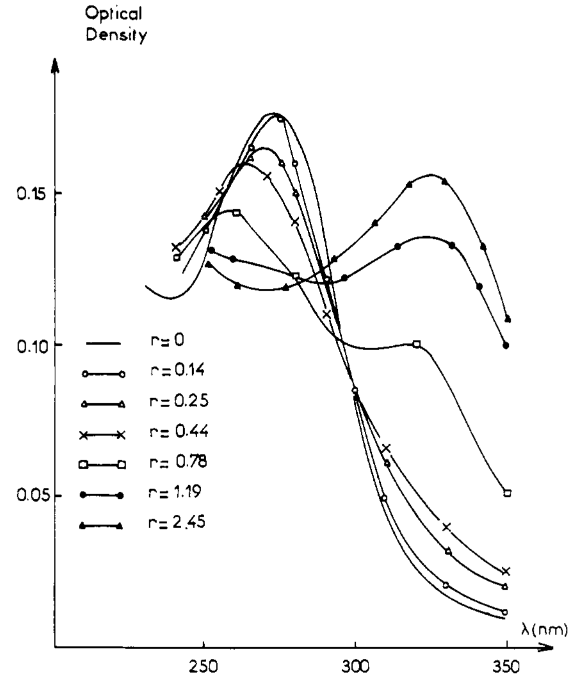


Figure 3. Evolution of the ultraviolet spectrum of polyisoprenyllithium as a function of r (TMEDA).

A major difference exists between these two complexing agents: if the existence of the complex $(OILi)_2 \cdot$PMDT is accepted, a structure like [OILi·PMDT] cannot be supported because the cis triplet is not shifted further for r values greater than 0.5.

It seems that the tertiary triamine (PMDT) possesses a lower complexation power than the diamine (TMEDA). Indeed, the delocalization of the negative charge in the living species is more important with TMEDA: the lowest chemical shift values of the cis triplet relative to oligoisoprenyllithium complexed with TMEDA and PMDT are, respectively, 3.30 and 3.85 (in ppm from Me_4Si). Consequently, TMEDA will disturb the microstructure of polyisoprene more than PMDT.[19]

3. Ultraviolet Spectroscopy of Oligoisoprenyllithium Complexed with TMEDA. Ultraviolet spectroscopy of oligoisoprenyllithium in cyclohexane solution shows only one absorption maximum at 273 nm in the absence of complexing agent (ϵ_{max} = 8000). In order to follow the evolution of the maximum by adding catalytic amounts of TMEDA, we have prepared polyisoprenyllithium initiated by *tert*-butyllithium in cyclohexane at 18 °C ([isoprene] = 7.5×10^{-2} mol·L^{-1}; [*t*-BuLi] = 3.8×10^{-4} mol·L^{-1}).

After complete initiation, checked by the constant optical density at 273 nm, increasing catalytic amounts of TMEDA were added at 18 °C. The ultraviolet spectra observed for different values of r and standardized for a living end concentration of 3.8×10^{-4} mol·L^{-1} are shown in Figure 3. It is found that the absorption maximum shifts from 273 to 257 nm. Simultaneously, the intensity of the absorption at 273 nm decreases and a shoulder develops with a new maximum between 320 and 325 nm.

The living complexed species is highly stable.

The shift from 273 to 257 nm appears to be complete at r = 0.5 and can be justified on the basis of the studies of Garton et al.[15] on polyisoprenyllithium in tetrahydrofuran. The species having trans and cis structures absorb at 305 and 287 nm, respectively.

However, it must be noted that the results of Garton et al.[15] concern monomeric living species but that in our case the species are associated. Nevertheless, according to the studies of these authors and according to our ^{1}H NMR data, it seems reasonable that the shift from 273 to 257 nm is evidence for trans/cis isomerization. The maximum at 273 nm corresponds to the trans isomer which predominates in nonpolar solvents but in the absence of any complexing agent. At 257 nm appears the peak of the cis isomer, which mainly exists in polar solvents or in the presence of TMEDA (in nonpolar solvents). This result is corroborated by our ^{1}H NMR experiments: the full isomerization observed through NMR and the maximum hypsochromic shift are reached for $r = 0.5$. Simultaneous decreasing of the optical density at 273 and 257 nm and the development of the shoulder between 320 and 325 nm can be explained by a change in the degree of association of polyisoprenyllithium.

In aliphatic solvents, polyisoprenyllithium has been reported to have an association number of 2[3,20–22] or 4.[23] The high complexing power of TMEDA allows the dissociation of the living species aggregates. More recently, Hadjichristidis and Roovers[24] have shown that the spectrum of the 1:1 polyisoprenyllithium/TMEDA complex has two maxima, one at 324 nm and the other at about 270 nm. At higher TMEDA-to-polyisoprenyllithium ratios a single sharp maximum at 324 nm is found. Slightly more than the stoichiometric amount of TMEDA is required to convert polyisoprenyllithium completely to the complex with a maximum at 324 nm. According to the same authors, the spectrum of 1:1 polyisoprenyllithium/TMEDA resembles that of polyisoprenyllithium (1×10^{-3} mol·L^{-1}) in a 1 M solution of tetrahydrofuran in hexane. Such spectra can be interpreted as being due to the coexistence of two types of polyisoprenyllithium end groups, one complexed and the other free. Both types of polyisoprenyllithium may be associated to different degrees.

In our case it seems reasonable to attribute the absorption maximum at 320 nm to a monomeric complexed form of polyisoprenyllithium.

In view of the controversy in the literature as to the initial state of aggregation, we think that the best schemes to fit our experiments are

$$(\mathrm{PILi})_n + 2n\mathrm{TMEDA} \rightleftarrows \underset{\mathrm{I}}{[(\mathrm{PILi})_2\cdot\mathrm{TMEDA}]_n}$$

$$[(\mathrm{PILi})_2\cdot\mathrm{TMEDA}]_n + n\mathrm{TMEDA} \rightleftarrows \underset{\mathrm{II}}{n\mathrm{PILi}\cdot\mathrm{TMEDA}}$$

Complex I takes into account the full isomerization observed by ^{1}H NMR and the ultraviolet spectroscopic results for $r = 0.5$ but does not exclude complex II, which justifies the NMR shift of the triplet corresponding to the living cis isomer upon increasing r from 0 to 1. Moreover, the existence of a monomeric 1:1 polyisoprenyllithium/TMEDA chelate is compatible with our kinetic results, where the order with respect to the active-species concentration is equal to 1.1, presuming that the PILi/TMEDA complex is monomeric.[19]

Results obtained by other investigators support this notion. Davidyan et al.[16] and Vinogradova et al.[25] attribute the ultraviolet absorption at 320 nm respectively to the nonaggregated 1:1 oligoisoprenyllithium/dimethoxyethane and polybutadienyllithium/TMEDA complexes; in both cases the absorptions at lower wavelengths correspond to aggregated forms of the living species. By dilution, temperature, and solvent effects in the presence of tetrahydrofuran, Roovers et al.[13] have shown evidence for the dissociation of polyisoprenyllithium, the nonaggregated species absorbing at 320 nm.

Finally, Dyball et al.[26] have shown that in the anionic polymerization of isoprene in diethyl ether with lithium as counterion, an increase in association of the living species is observed upon increasing its concentration.

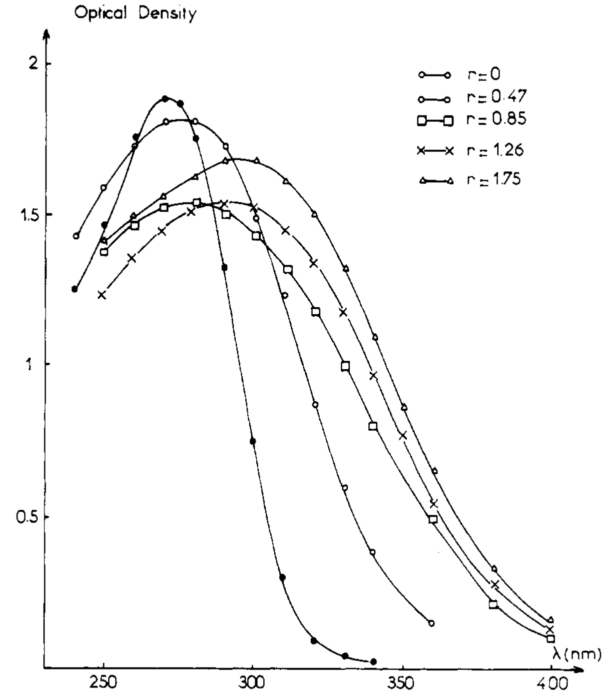
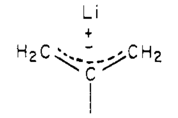


Figure 4. Evolution of the ultraviolet spectrum of polyisoprenyllithium as a function of r (PMDT).

Remark: Polyisoprenyllithium complexed with TMEDA can be obtained by polymerizing isoprene in the presence of the tertiary diamine or by adding TMEDA to the living polymer. In both cases no change of the ultraviolet spectrum is observed with time. Thus, the absorption at 320 nm cannot be attributed to an isomerized species like



arising from a readjustment of the 4,3-addition, as observed in tetrahydrofuran.[15]

4. Ultraviolet Spectroscopy of Oligoisoprenyllithium Complexed with PMDT. The evolution of the ultraviolet spectrum as a function of r = [PMDT]/[living ends] is shown Figure 4. At first sight, only one absorption is manifest. For r values lower than 1, the maximum moves between 273 and 276 nm; thus, with an increase in the amount of catalytic PMDT, a slight bathochromic effect and a widening of the absorption band at high wavelengths are observed. Even for very low r values, no hypsochromic effect can be observed, although trans/cis isomerization is evident. For r values greater than 1, a wide absorption band with a maximum at 290 nm appears, but no shoulder develops at 320 nm; it seems that different aggregated and nonaggregated living species must exist in the medium.

Remarks: The evolution of the ultraviolet spectrum as a function of r has been followed for two very different living species concentrations: a "low" one (4×10^{-4} mol·L^{-1}) and a "high" one (10^{-2} mol·L^{-1}). In both cases the absorption bands are identical; no change with time is observed.

Conclusion

Ultraviolet data for the chelates polyisoprenyllithium complexed respectively with TMEDA and PMDT are summarized in Figure 5. TMEDA shows two absorptions at 257 and 320 nm, respectively, attributed to the aggre-

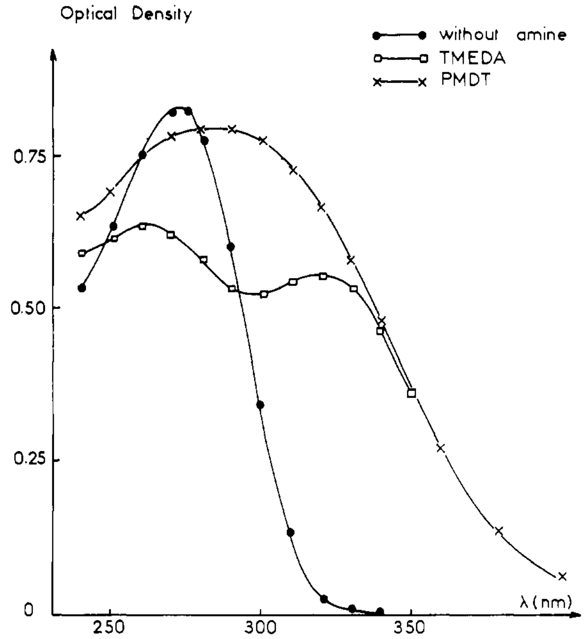


Figure 5. Ultraviolet spectra of polyisoprenyllithium complexed with TMEDA and PMDT ($r = 1$; $T = 18$ °C, [PILi] = 5×10^{-3} mol·L^{-1}).

gated and the monomeric species.

Increasing catalytic amounts of PMDT give a slight bathochromic effect (from 275 to 290 nm) and a widening of the absorption band at higher wavelengths, indicating the existence of the nonaggregated 1:1 chelate. In the case of PMDT, the low resolution of the spectra is probably owing to species like $[(\mathrm{PILi})_2\cdot\mathrm{PMDT}]_n$ and the other unknown structures.

The ultraviolet data, at least in the case of TMEDA, are well supported by the NMR (and the kinetic) results. The full trans/cis isomerization observed at $r = 0.5$ can be explained by means of a species like $[(\mathrm{PILi})_2\cdot\mathrm{TMEDA})]_n$.

Experimental Part

Materials. (a) Monomer. Isoprene (Fluka, purum) was distilled over calcium hydride, degasified on a vacuum line (10^{-6} mmHg), and prepolymerized on *n*-butyllithium. Stored over calcium hydride and under high vacuum, the monomer was again prepolymerized before use.

(b) Initiator. *tert*-Butyllithium (Fluka) was sublimed at +70 °C under high vacuum. The initiator can then be stored for several days at −30 °C before use after dissolution in degasified benzene or cyclohexane.

(c) Complexing Agents. TMEDA and PMDT (Merck) were distilled over calcium hydride. Then they were distilled and stored on molecular sieves under high vacuum (10^{-6} mmHg).

(d) Solvents. Benzene and cyclohexane were treated respectively with sulfuric acid and with a 1:1 mixture of sulfuric and nitric acids. After washing with a concentrated solution of potassium hydroxide and distilled water, the solvents were dried over calcium chloride and distilled from potassium. After degasifying under high vacuum (10^{-6} mmHg), the solvents were stored first over calcium hydride and then over *n*-butyllithium. Trace aromatic hydrocarbons can be removed from the cyclohexane, if necessary, by silica gel treatment.

Oligomerization and Polymerization Procedure. The reactions were carried out under high vacuum (10^{-6} mmHg) in sealed glass vessels. Each apparatus was carefully washed with a hydrofluoric acid solution and distilled water (in the case of oligomerization) or with a benzene solution of *n*-butyllithium and benzene (in the case of polymerization).

(a) Oligomerization. Isoprene was slowly distilled into a benzene solution of *tert*-butyllithium under energetic stirring at room temperature (~18 °C). The following conditions were employed: [isoprene]/[*tert*-butyllithium] = 1.2, [*tert*-butyllithium] = 1.0 mol·L^{-1}, time of reaction = 24 h.

Samples of oligoisoprenyllithium for NMR were prepared under high vacuum after replacing protonated benzene by deuterated benzene and the complexing agent. The spectra were recorded on a Varian HA-100 spectrometer as a function of r at room temperature. $\mathrm{Me_4Si}$ was used as an internal reference (lock: benzene).

(b) Polymerization. The polymerization was carried out under high vacuum in an apparatus supplied with an ultraviolet cell; the spectra were recorded on a Cary 118C spectrometer. The addition of the monomer to a cyclohexane solution of the initiator affords polyisoprenyllithium, the absorption of which appears at 273 nm. The optical density at that wavelength was followed until complete consumption of the initiator. Then ultraviolet spectra were recorded as a function of increasing catalytic amount of complexing agent. Complexed polyisoprenyllithium shows a high stability over time at room temperature (18 °C).

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