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Polymer Structure and Complexes in the Lithium Alkyl Initiated Polymerization of Isoprene in the Presence of 1,2-Dipiperidinoethane†

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ABSTRACT: A study of the complexes formed between lithium and 1,2-dipiperidinoethane in oligomeric active chains of polyisoprene is reported. A comparison of NMR and electronic spectra indicates little drift of complex distribution over a wide concentration range. No major differences in behavior were found between the present NMR results and those reported on a simple one-unit growing chain with a *tert*-butyl end group. The results offer confirmatory evidence for the validity of a mechanism suggested on the basis of NMR studies on the one-unit model. This involved solvated tetrameric, dimeric, and monomeric forms of the organolithium intermediates. The effect of the presence of both 1,4- and 4,1-type chain ends on polymer microstructure is discussed.

Lithium alkyl initiated polymerizations of dienes give largely 1,4 polymers when carried out in hydrocarbon solvents, but polymers with a high percentage of vinyl unsaturation in polar solvents. Specific polar cation-solvating molecules, however, effect the same change when present in much smaller amounts. In 1966 Langer[1] described the preparation of highly 1,2-polybutadiene in systems containing a chelating diamine of the type $Me_2N(CH_2)_nNMe_2$ present in equimolar amount to the lithium alkyl. Tetramethylethylenediamine (TMEDA, $n = 2$) was particularly effective since polymerizations carried out at 0 °C in its presence gave a polymer containing over 80% 1,2 structures. It is also effective in isoprene polymerization, producing polymers of greater than 70% vinyl content at TMEDA/Li ratios around unity[2] at 18 °C. 1,2-Dipiperidinoethane (DIPIP) is even more effective in butadiene polymerization, producing close to 100% 1,2-polybutadiene when present in an equimolar ratio to lithium in a polymerization carried out at 5 °C.[3-5] Preliminary experiments suggested that it was however less effective in inducing vinyl structures in polyisoprene.[5] In order to elucidate the factors governing the stereoregulation process, spectroscopic examinations (NMR and UV-visible) of oligomeric products from both butadiene and isoprene have been carried out. Results on the isoprene/TMEDA system have been reported,[2,6] and recently the complexes formed with DIPIP and the single-unit adduct of *tert*-butyllithium and isoprene have described.[7] In this paper we present NMR data on oligomers of somewhat longer chain length together with their electronic spectra measured at concentrations much lower than those necessarily used in NMR work and equivalent to those used under polymerization conditions.

Experimental Section

Isoprene (Fluka puriss or Phillips Research Grade), benzene, hexane, cyclopentane, and 1,2 dipiperidinoethane (Aldrich) were purified and dried as described previously[6,7] and stored under vacuum. The preparation of a 1:1 adduct of *tert*-butyllithium and isoprene has been adequately described earlier.[8] In the present investigation the preparation of an oligomer of DP ~ 3 was carried out in the same manner by simply increasing the isoprene-to-*tert*-butyllithium ratio. This material was used in benzene for the NMR study at a concentration ~1.0 M. The oligomers used for the study of electronic spectra were made via the preparation of the single-unit diisoprenyl mercury compound,[9] which was cleaved by lithium suspension in cyclopentane to form the 1:1 *tert*-butyllithium adduct with isoprene. Four more isoprene units were added to form an oligomeric lithium compound of DP ~ 5. All manipulations were made under vacuum with prewashed apparatus for studies in the dilute range (less than 0.5 M).

The samples for NMR study were prepared by replacing the benzene used in their preparation by deuteriobenzene and varying amounts of 1,2-dipiperidinoethane. The spectra were recorded on a Varian HA-100 instrument, the signals from residual undeuterated benzene serving as reference. Polymerizations were initiated by *n*-butyllithium in the presence of the diamine in cyclohexane at room temperature. The microstructures of the polymers produced were measured by ^1H NMR in deuteriobenzene with a Bruker AM-400 instrument. The analysis method was that described by Assioma[10] involving the olefinic signals at δ 5.82 (—CH═ 1,2), 5.27 (—CH═ 1,4), and 5.00 + 4.85 (═CH_2 1,2 and 3,4 unresolved). UV spectra were recorded on a Cary 210 spectrophotometer at lithium concentrations of $\sim 1.5 \times 10^{-2}$ and $\sim 1.5 \times 10^{-4}$ M. Quartz cells (1 cm) fused to the preparative glassware were provided with a 0.99-cm spacer that could be moved magnetically in or out of the optical path as required. A correction for DIPIP absorption was made for measurements below ~250 nm.

Results

The NMR measurements on the oligomeric isoprenyllithium are illustrated in Figures 1 and 2. The chemical shifts of the γ-protons are particularly sensitive to the local environment of lithium and separate into individual signals from cis and trans forms, which under these conditions are not expected to interconvert on the NMR time scale. Rapid equilibration occurs at room temperature between the different aggregated species so that one expects an averaged signal for both cis and trans forms. The lower field γ-signal is attributed to the trans forms at low or no DIPIP, the higher field to cis forms.[11,12] The trans signal moves more rapidly upfield at increasing DIPIP ratios (R), passing the cis signal at $R \sim 0.8$ and becoming the high-field signal at higher R values. At the same time the percentage of trans material varies with DIPIP ratio as shown in Figure 2. Starting at 65% at $R = 0$, it drops to ~30% at $R \sim 1$ and subsequently increases back to

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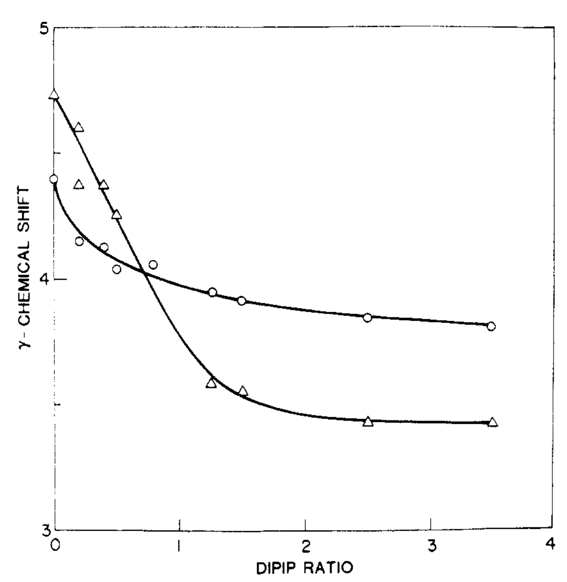

Figure 1. Proton chemical shifts of cis (○) and trans (△) γ-carbons of oligomeric isoprenyllithium in deuteriobenzene at room temperature.

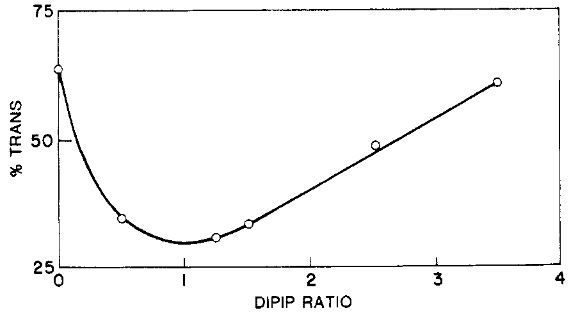

Figure 2. Percentage of trans active centers (determined from ^{1}H spectra) of oligomeric isoprenyllithium in benzene as a function of *R*.

~65% at *R* ~ 3.5. The situation is entirely similar to that reported for the simple 1:1 adduct of *tert*-butyllithium and isoprene in cyclopentane,[7] differing only in that beyond the minimum, the percentage of trans species increases to higher levels in the present case. With both compounds, however, unlike experiments in which TMEDA is used where only cis species can be observed at *R* > 0.5, cis and trans isomers exist at all measured *R* values.

It is clear from earlier work[7] that at least three different complexes can occur, whose relative concentrations may change with dilution. The characteristic near-UV absorption band of the active centers was therefore studied at lithium concentrations ~10^{-2} and ~10^{-4} M, i.e., in the range of initiator concentrations useful in polymerization. These spectra are again sensitive to the lithium environment (Figures 3 and 4). At either concentration, the original absorption band, whose position is somewhat concentration dependent,[13] broadens and then shifts to shorter wavelength to *R* ~ 0.5. At higher *R*, a shoulder grows in the region ~325 nm and the 255-nm maximum decreases. These observations are similar to those obtained with TMEDA as complexing agent[2,6] except that, for the present experiments, the long-wavelength absorption does not fully develop at equivalent large *R* values. This is consistent with the idea that with the isoprenyllithium–DIPIP system a solvated unassociated lithium compound is never completely formed as will be seen later.

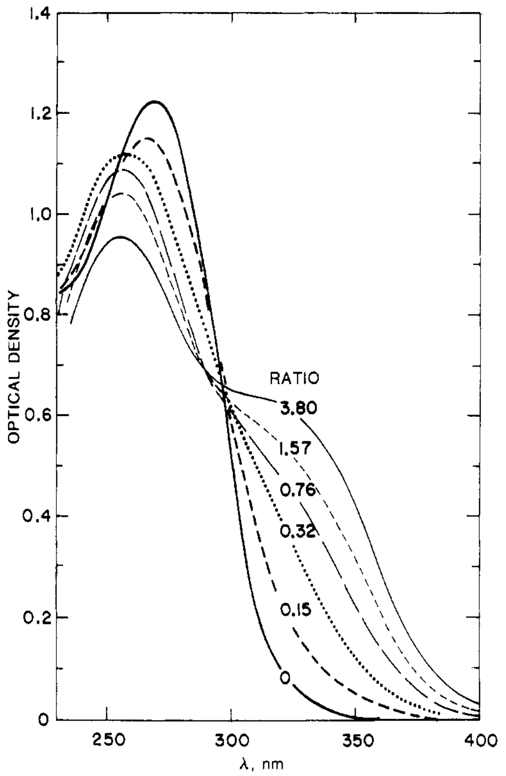

Figure 3. UV-visible spectra of the active centers at an isoprenyllithium concentration of 1.5 × 10^{-2} M as a function of DIPIP ratio (cyclopentane).

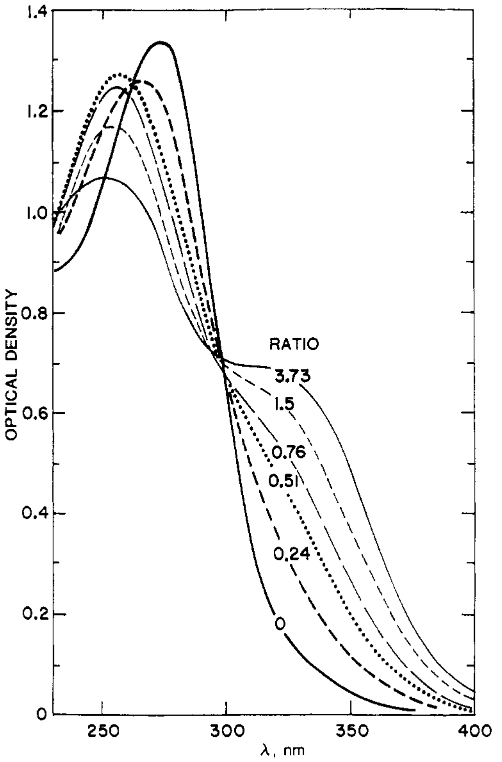

Figure 4. UV-visible spectra of the active centers at an isoprenyllithium concentration of 1.5 × 10^{-4} M (cyclopentane).

The microstructure changes with DIPIP ratio for polymerization in cyclohexane at ~20 °C and an initiator concentration of 10^{-2} M is shown in Figure 5. For comparison purposes the effect of TMEDA under exactly the same experimental conditions is reported. The limiting percentage of 3,4 structures at high DIPIP ratio is close to that observed with TMEDA. The relative amounts of the minor components are however inverted; more 1,2 and less 1,4 structures are found with DIPIP, although their presence is detected only at a slightly higher DIPIP ratio.

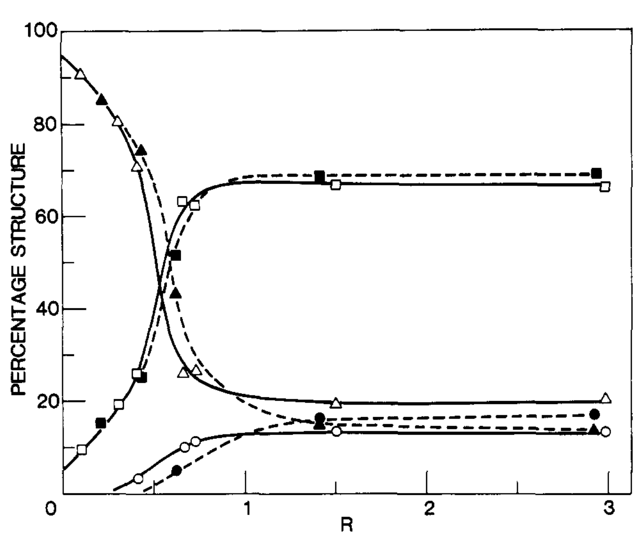

Figure 5. Microstructure of polyisoprenes produced in cyclohexane at 22 °C in the presence of TMEDA (open symbols) or DIPIP (closed symbols). Structure: (□) 3,4; (△) 1,4; (○) 1,2.

Discussion

The strong similarity between the present ^{1}H NMR results and those previously obtained on the 1:1 adduct (t-Bu-$CH_2CHC(CH_3)CH_2Li$) suggests that the type of complexes appearing in the oligomeric isoprenyllithium system must be very similar to those suggested in the former case. The sole difference is that the final percentage of what was described as a trans monosolvated organolithium species is higher in the oligomer case. This appears to be caused by the use of benzene as solvent for the oligomeric compound rather than the cyclopentane used in the study of the 1:1 *tert*-butyllithium adduct. A check at $R = 3$ showed that the oligomeric isoprenyllithium in cyclopentane also only gives ~35% trans species, close to the percentage found earlier for the model one-unit chain. Similar differences in aggregate dissociation have been observed previously between aliphatic and aromatic solvents for unsolvated polyisoprenyllithium.[13]

The study of electronic spectra of allylic lithium compounds offers two main advantages. Firstly, their concentration can be in the range used in actual polymerizations and second, the optical time scale is so short that averaged absorptions can be excluded. The observed spectrum will be the sum of those of the individual species. Unfortunately band attribution is more difficult and more overlap occurs than in NMR signals. As noted above, the spectra shown in Figures 3 and 4 are very similar to those observed in the presence of TMEDA[2,6] so that the same attribution is likely to hold. The initial shift of the absorption maximum to ~255 nm can be attributed[6] to the formation of the monosolvated cis dimer. Such a hypsochromic effect is consistent with a general trend that cis species of allylic alkali metal systems absorb at shorter wavelength.[15,16] The intermediate formation of a monosolvated tetramer is hard to detect but may be represented by the very initial broadening observed in Figure 3 at $R = 0.15$. The final buildup of the shoulder ~325 nm can be similarly attributed to the monosolvated monomeric species as before.[6] The weakness of this signal even at $R = 3.5$ as compared with the TMEDA case where a strong isolated band is formed already at $R = 2$ is in agreement with the NMR evidence that monomeric solvated species are much more readily formed with TMEDA than DIPIP. The percentage of monomeric species is, however, still increasing at $R \sim 3.5$ so that at very high DIPIP ratios (~15) an isolated absorption band (λ_{max} 327 nm) is observed, indicating more complete dissociation.

It is at first rather surprising that this interpretation based on NMR evidence on solutions of quite high concentration fits at least semiquantitatively with the appearance of the electronic spectra; i.e., the shift to 255 nm is complete at $R = 0.5$ even at 1.5×10^{-4} M lithium. Moreover, there is no obvious major difference in the evolution of spectra with R between the spectra at 1.5×10^{-2} and 1.5×10^{-4} M concentrations of the lithium compound. Nor did any obvious difference become evident when the experiments were repeated at −20 °C. Generally the equilibria cannot be very concentration or temperature dependent in the ranges studied. The equilibria suggested to occur previously from NMR evidence on the 1:1 isoprene/lithium adduct were as follows:

$$\mathrm{T} + \mathrm{d} \overset{K_1}{\rightleftharpoons} \mathrm{T{:}d} \qquad (\mathrm{T{:}d} \equiv \text{solvated tetramer}) \tag{1}$$

$$\mathrm{T{:}d} + \mathrm{d} \overset{K_2}{\rightleftharpoons} 2\mathrm{D{:}d} \qquad (\mathrm{D{:}d} \equiv \text{solvated dimer (cis)}) \tag{2}$$

$$2\mathrm{D{:}d} + 2\mathrm{d} \overset{K_3}{\rightleftharpoons} 4\mathrm{M{:}d} \qquad (\mathrm{M{:}d} \equiv \text{solvated monomer (trans)}) \tag{3}$$

Note that only in equilibrium 1 does the number of species change; hence all equilibria except this one are expected to be uninfluenced by total lithium concentration. If, therefore, K_1 is rather large, i.e., a strong complex is formed between the original tetramer and complexing agent, then little concentration-induced variation in the fractions of the four species will occur.

Attempts to correlate the evidence on the major complexed species present under a given set of conditions with the polymer microstructure observed under the same conditions can be a difficult task for two reasons. First of all, the models used in the above analysis are essentially 4:1 chain ends ($\sim CH_2CHC(CH_3)CH_2Li$) produced by oligomerizations carried out in benzene or cyclopentane whereas the presence of appreciable fractions of 1,2 structures in the polymer formed indicates that 1,4 active centers ($\sim CH_2C(CH_3)CH_2CH_2Li$) must exist in polymerizations carried out in the presence of chelating diamines. There is not necessarily a simple connection between the type of complex present and the polymer produced by the system. Only if each species has about the same reactivity toward monomer would a close correlation be expected. One highly reactive individual complex present in quite small amount would destroy any obvious correlation. Some discussion could, however, be profitable. In the presence of both DIPIP and TMEDA at 10^{-2} M lithium, the polymer microstructure remains quite highly 1,4 at low R values. Only between $R = 0.4$ and 0.7 does a rapid microstructure change occur. The results are very similar to those reported previously on isoprene polymerization[14] at a much lower lithium concentration (3.5×10^{-4} M) in the presence of TMEDA. Again the behavior is not very sensitive to concentration changes. It appears to be characteristic of this monomer and contrasts with that observed in butadiene polymerization with either DIPIP[17] or TMEDA[18] where at $R \sim 0.3$ the polymer microstructure is highly vinyl in nature.

The retention of 1,4 structures in polyisoprene to much higher diamine/lithium ratios must be related to the persistence of the normal polymerization process present in hydrocarbon solvents (i.e., via unsolvated organolithium compounds). Both the percentage of 1,4 and the highly cis nature of those units (~80%) are in agreement with this idea, as is the fact that 1,2 structures only become detectable at $R > 0.4$. This phenomenon can occur to quite large extents of depletion of the unsolvated aggregated polyisoprenyllithium species due to the low reaction order ($\sim^1/_4$). Thus at 90% depletion of the original tetramers via complex formation of the type indicated above, the rate of the normal process is still roughly half that in the absence of complexing agent. Since the rate of isoprene polymerization in the absence of diamines is relatively high, effective competition occurs with solvated species until nearly all are in this form. On the other hand, the lithium-based polymerization of butadiene in hydrocarbon solvents is considerably slower than observed with isoprene.[19] In this case although the unsolvated aggregates still persist, they compete less effectively with solvated species of presumably approximately the same reactivity as in isoprene polymerization. The result is that the microstructure change of polybutadiene becomes effective at very low values of R with both diamines.

At values of $R \sim 3$, Figure 5 shows that DIPIP is somewhat more efficient than TMEDA at stimulation of vinyl unsaturation (88% vs. 80%), but still less so than in butadiene polymerization. It is possible that these observations are related to the mixture of 1,4 and 4,1 active chain ends present. If the former resemble solvated butadienyl anion pairs, they will be unassociated, in the trans configuration and give very highly 1,2 polymer.

The 4,1 chain ends, however, according to the model compounds studied will be only partly dissociated to the trans form at this point. Appreciable amounts of cis dimers will remain. Evidence has been presented that the cis active centers are somewhat less vinyl stereospecific.[5] TMEDA solvation will produce a greater fraction of cis active centers for the 4,1 active centers will be entirely cis[6] and if butadiene active centers are again taken as models for 1,4 active chain ends, these will be about 60% cis.[18] The order of vinyl unsaturation expected would be DIPIP:butadiene > DIPIP:isoprene > TMEDA:isoprene, as observed.

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Hydrochlorination of *trans*-1,4-Polyisoprene Lamellas

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ABSTRACT: Lamellas of synthetic *trans*-1,4-polyisoprene in the α form, prepared by precipitation from amyl acetate solution, were reacted in suspension using an excess of HCl at −7 to −10 °C for various times. The resulting copolymers were quantitatively analyzed by 50.32-MHz carbon-13 NMR spectroscopy using assignments made with the aid of solution-hydrochlorinated samples; the average number of monomer units in the reacted ($\langle B \rangle$) and unreacted ($\langle A \rangle$) blocks was obtained. When the reaction is carried out in acetone using lamellas grown at crystallization temperatures (T_c) of 20 and 30 °C, $\langle B \rangle$ remains constant after 1–2 days of reaction and has a value of 4.8 ± 0.3; the average value of $\langle A \rangle$ increases with T_c. The fraction hydrochlorinated in acetone is approximately half the noncrystalline fraction calculated from density measurements. Hydrochlorinated lamellas, dissolved in $CDCl_3$, in 4-methyl-2-pentanone, or in heptane and precipitated by solvent evaporation or by cooling, were found by X-ray diffraction to be noncrystalline. When hydrochlorination was carried out in amyl acetate suspension, the results obtained suggest that penetration of the crystal core occurs, particularly at T_c's of 10 and 20 °C. Wide-angle X-ray diffraction studies show the presence of some completely hydrochlorinated material in the products.

Introduction

The crystallization of *trans*-1,4-polyisoprene (TPI) from solution leads to overgrown lamellas or lamellar structures in the α or β forms, depending on the conditions used.[1–5] The epoxidation of *trans*-1,4-polydiene lamellas[3,6–10] and lamellar structures[4,11] in suspension, particularly in conjunction with carbon-13 solution NMR,[9,10] has been used to examine, in a quantitative fashion, the nature of the surfaces. The selective reaction of the double bonds at the lamellar surfaces leads to a segmented block copolymer in which the reacted blocks correspond to the original chain folds, noncrystallizing chain ends, and any exposed lateral surfaces. If complete reaction occurs at the lamellar surfaces only, and if the noncrystallizing chain ends and lateral areas are small, carbon-13 NMR analysis of the

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