Anionic polymerization of isoprene by the complexes oligoisoprenyllithium/tertiary polyamines in cyclohexane: 3. Structural study of the polymers by ^{1}H n.m.r. at 100 MHz

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The microstructure of polyisoprene prepared anionically in the presence of catalytic amounts of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and pentamethyldiethylenetriamine (PMDT) has been studied as a function of $r=$[TMEDA]/[living ends] and $r=$[PMDT]/[living ends]. No significant effect is observed for $r \leqslant 0.5$. The structure varies drastically for $r > 0.5$. The 4,3 addition increases mainly at the expense of the *cis*4,1 addition and a plateau is reached for $r \geqslant 1.0$. The results are discussed on the basis of the nature of the living species.

Keywords Protonic nuclear magnetic resonance; polyisoprene; anionic

INTRODUCTION

The influence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and pentamethyldiethylenetriamine (PMDT) on the kinetics of the anionic polymerization of isoprene in cyclohexane has already been studied[1]. It has been shown that these two tertiary polyamines can decrease or increase the propagation rate, depending on the concentration range. The results have been discussed on the basis of the nature of the living species.

The nature of oligoisoprenyllithium complexed with TMEDA or PMDT was also investigated[2] by protonic nuclear magnetic resonance and ultra-violet spectroscopy as a function of $r=$[tertiary polyamine]/[living ends]. ^{1}H n.m.r. showed 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 u.v. spectra confirmed the n.m.r. results and gave information about the association of the living species.

The purpose of this paper is to present some results relative to the structure of the polymers obtained by polymerizing isoprene by means of oligoisoprenyllithium complexed with TMEDA and PMDT in cyclohexane.

Indeed the nature of the solvent, the counter-ion and the complexing agent, as well as the temperature, determine the structure of polydienes obtained by anionic polymerization. ^{1}H n.m.r. is then an efficient tool to characterize the polymers. In a non-polar medium the living end presents a 4,1 (*cis* and/or *trans*) configuration, but 4,1 and 1,4 structures are observed in a polar solvent since the dead polymer shows respectively an appreciable content of 4,3 and 1,2 links. Indeed the next entering monomeric unit determines the structure of the last deactivated unit as depicted below:

living end structure→deactivated unit structure

4,1 (*cis* and/or *trans*)→4,1 (*cis* and/or *trans*) + 4,3

1,4 (*cis* and/or *trans*)→1,4 (*cis* and/or *trans*) + 1,2

The distinction between 1,4 and 4,1 addition is only possible for oligomers but not for high polymers. In the latter case, we shall speak indifferently of 1,4 or 4,1 structures, but a mixture of both is really present.

Several workers have studied the structure of polybutadiene and polyisoprene obtained anionically in the presence of TMEDA. Hay *et al.*[3] consider the existence of an active complex like [polybutadienyllithium·(TMEDA)$_2$] which they suggest is a separated ion-pair leading to 70–90% 1,2 links in the polymer. Antkowiak *et al.*[4] do not observe any variation of structure for a ratio $r=$[TMEDA]/[living ends]>1; the active species should here be the complexed contact ion-pair [polybutadienyllithium·TMEDA].

On the other hand, Vinogradova *et al.*[5] confirm the results of Antkowiak. Essel[6] has polymerized isoprene in hexane and in the presence of TMEDA; for a ratio $r=1$, the polymer structure suggests, according to him, a propagating species like a separated ion-pair (25% 4,1; 30% 1,2; 45% 4,3). Erussalimsky *et al.*[7] have studied the

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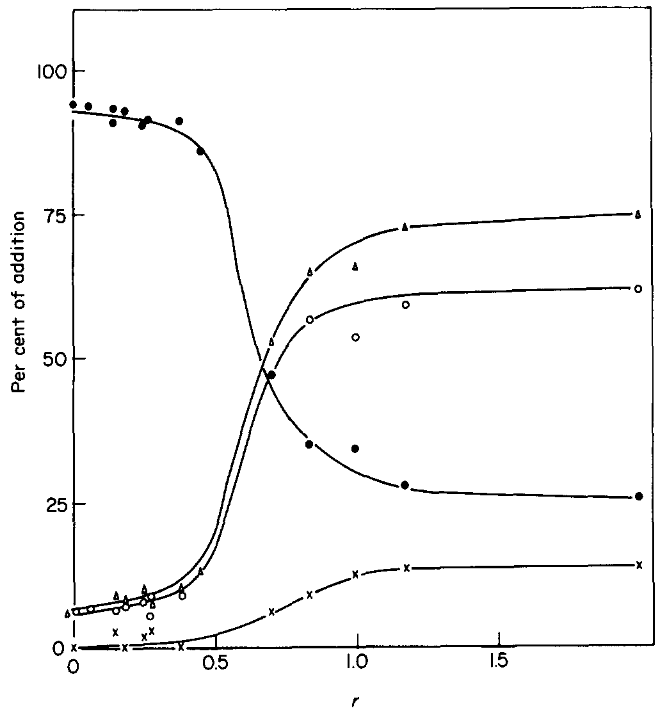


Figure 1 Variation of the polyisoprene structure as a function of r = [TMEDA]/[living ends] ([living ends] = 3.5 x 10^{-4} mol l^{-1}): ●, total 4,1; ○, 4,3; x, 1,2; △, 1,2 + 4,3

variation of the 3,4 structure in polyisoprene as a function of r; a plateau is reached for $r = 4$ (about 70% 3,4 addition).

Finally the conclusions of Smid[8] do not agree with the results of Hay[3] and Essel[6]. It is well known that the aptitude to lead to separated ion-pairs is enhanced by the possibility of charge delocalization. Smid[8] observes only contact ion-pairs in the case of the highly delocalized fluorenyllithium in pure TMEDA. So the most credible species in the system polyisoprenyllithium/TMEDA/hexane (or cyclohexane) must be a contact ion-pair, since the delocalization is less important in polyisoprenyllithium than in fluorenyllithium.

EXPERIMENTAL

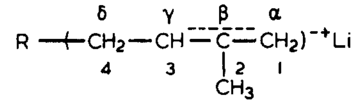
The purification of chemicals, the synthesis and the study of the living species using ^{1}H n.m.r. and u.v. spectroscopy have been described in detail in other papers[1,2]. The ^{1}H n.m.r. spectra of the dead polyisoprene were recorded at 100 MHz at approximately 60°C on a Varian HA 100 spectrometer. The polymer samples were dissolved in deuterated benzene; TMS and protonated benzene were added to the mixture.

RESULTS AND DISCUSSION

Isoprene has been polymerized anionically using oligoisoprenyllithium/TMEDA and PMDT complexes in cyclohexane at room temperature. In order to explain the variation of the polymer structure as a function of r, we first studied the nature of the living complexed species[2].

^{1}*H n.m.r. of oligoisoprenyllithium (OILi) complexes*

OILi with TMEDA. An oligoisoprenyllithium of polymerization degree equal to 1.2 is synthesized under vacuum. The living species in solution in C_6D_6 is characterized at room temperature by ^{1}H n.m.r. at 100 MHz, and its behaviour will be roughly the same in cyclohexane. The living oligomer is generally described by the following delocalized structure:



$$R \text{---}\!\!\!(\overset{\delta}{\underset{4}{CH_2}} - \overset{\gamma}{\underset{3}{CH}} \overset{\beta}{\underset{\underset{CH_3}{|\,2}}{=\!=C=\!=}} \overset{\alpha}{\underset{1}{CH_2}})^{-\,+}Li$$

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

Addition of TMEDA to oligoisoprenyllithium induces important changes:

(1) The two triplets are shifted upfield by increasing r from 0 to 1.

(2) Simultaneously, a *trans–cis* isomerization occurs and the *cis* triplet only is observed for $r \geqslant 0.5$.

The upfield shift points to an increase of the electronic density on the γ carbon as shown in polar solvents. In parallel an increase of 4,3 and 1,2 links should be observed in the polymer. On the other hand, complete isomerization for $r = 0.5$ suggests the complexation of all living ends, the oligoisoprenyllithium (OILi) then having the dimeric structure [$(OILi)_2$.TMEDA]. However, the maximum shift is reached for $r = 1$, suggesting the presence of a species like [OILi.TMEDA] at higher ratios.

OILi with PMDT. The ^{1}H n.m.r. study of oligoisoprenyllithium complexed with PMDT shows two important effects as observed in the case of TMEDA:

(a) an upfield shift of the two triplets (γ proton), and

(b) a *trans–cis* isomerization.

However, in the case of PMDT a slight difference in behaviour appears. It seems that for r = [PMDT]/[living ends] $\geqslant 0.5$, no 'sensible' shift of the *cis* triplet is observed. Full isomerization at $r = 0.5$ suggests the existence of the species [$(OILi)_2$.PMDT]. A major difference exists between both complexing agents: if the existence of the complex [$(OILi)_2$.PMDT] can be suggested, no evidence for a structure like [(OILi).PMDT] can be obtained by n.m.r. because the *cis* triplet is not further shifted for r values higher than 0.5. Other evidence, however, principally u.v.–visible spectroscopy, shows that further changes do in fact occur above $r = 0.5$. It seems that PMDT possesses a lower complexation power than 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 OILi complexed with TMEDA and PMDT are respectively 330 and 385 (δ in cps from TMS). Consequently TMEDA disturbs the microstructure of polyisoprene more than PMDT.

Variation of the polyisoprene structure as a function of r

r = [*TMEDA*]/[*living ends*]. With increasing values of r the 4,3 addition increases at the expense of the total 4,1 addition (*Figure 1*), mainly at the expense of the *cis* 4,1 addition (*Figure 2*). The small percentage of 1,2 structures present ($\leqslant$ 14%) suggests that very few 1,4 groups occur in the polymer since 1,4 chain ends in the presence of TMEDA are more likely to form vinyl structures. The polyisoprene microstructure does not vary for $r \geqslant 1$ (25% 4,1; 61% 4,3; 14% 1,2).

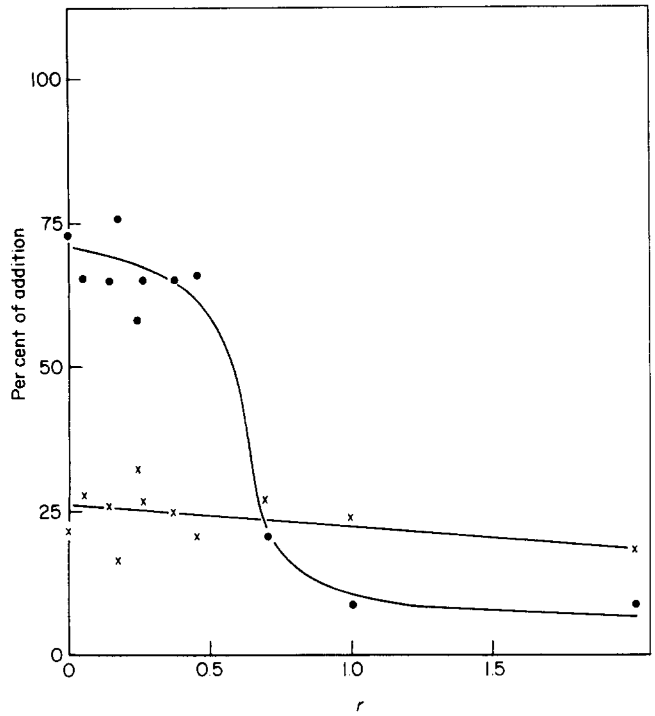


Figure 2 Variation of the *cis* and *trans* 4,1 content as a function of r = [TMEDA]/[living ends] ([living ends] = 3.5 x 10^{-4} mol l^{-1}): ●, *cis* 4,1; x, *trans* 4,1

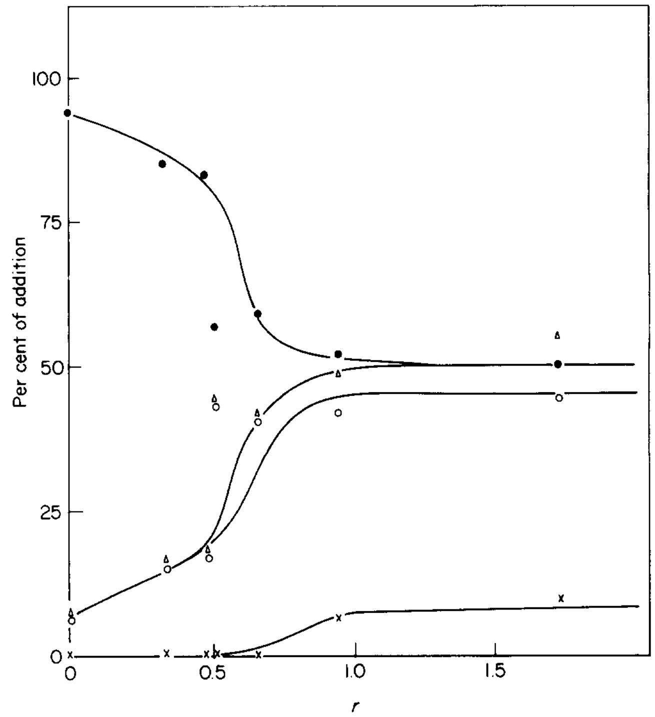


Figure 3 Variation of the polyisoprene structure as a function of r = [PMDT]/[living ends] ([living ends] = 4.5 x 10^{-4} mol l^{-1}): ●, total 4,1; ○, 4,3; x, 1,2; △, 1,2 + 4,3

For $r \leq 0.5$ the microstructure is not significantly affected by catalytic amounts of TMEDA (*Figure 1*), but the microstructure varies drastically for $r > 0.5$, accounting for the presence of [(polyisoprenyllithium)$_2$.TMEDA] as depicted in the n.m.r. study of the living oligomers. On the other hand, the existence of the species like [polyisoprenyllithium.TMEDA] has to be taken in account since the microstructure varies up to $r = 1$. These results agree well with Antkowiak's[4] conclusion.

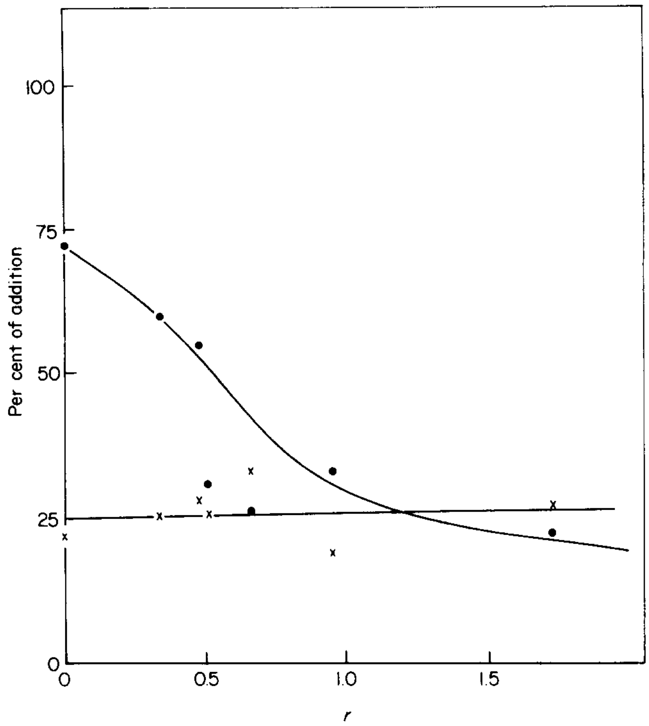


Figure 4 Variation of the *cis* and *trans* 4,1 content as a function of r = [PMDT]/[living ends] ([living ends] = 4.5 x 10^{-4} mol l^{-1}): ●, *cis* 4,1; x, *trans* 4,1

It is interesting to compare our results with some other published data[3,6]. Essel[6] advocates a separated ion-pair as active species. In agreement with Smid[8], we favour more a contact ion-pair with a donor doublet. Finally the observations do not give evidence for a separated ion-pair like [(polyisoprenyllithium).TMEDA$_2$] which has been assumed to be active in the polymerization of butadiene[3].

r = [PMDT]/[*living ends*]. As expected, PMDT shows an analogous behaviour to TMEDA but less pronounced (*Figures 3* and *4*) due to its lower complexation power. Increasing the catalytic amount of PMDT increases the 4,3 addition at the expense of the total 4,1 addition (mainly of the *cis* 4,1). Again a very low (~7%) quantity of 1,2 structure is present and suggests small amounts of 1,4 addition.

The microstructure of polyisoprene is slightly affected for $r \leq 0.5$ but a significant change is observed for $r > 0.5$. A plateau is reached for $r \geq 1.0$.

The results can be discussed on the basis of species like [(polyisoprenyllithium)$_2$.PMDT] and [(polyisoprenyllithium).PMDT] as in the case of TMEDA. Only the ratio between the different species should be different for a given value of r. Finally the u.v. study[2] has given evidence that TMEDA dissociates the living species more than PMDT, showing the lower complexation power of the triamine.

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