# Nuclear Magnetic Resonance Studies of the Propagating Chain End in the Organolithium Polymerization of Dienes. II. Isoprene and 2,3-Dimethylbutadiene in Hydrocarbon Solvents

**Maurice Morton,* R. D. Sanderson,† R. Sakata,‡ and L. A. Falvo§**

*Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.*

*Received September 5, 1972*

ABSTRACT: High-resolution studies have been carried out on the organolithium polymerization of isoprene and 2,3-dimethylbutadiene in hydrocarbon solvents. As in the case of the previously reported butadiene polymerization, no evidence could be found of any measurable amount of complexation of the isoprene with the organolithium chain end. The proton resonance spectrum of the *chain-end unit* in the case of isoprene indicates an exclusively 4,1 structure, rather than a 1,4 (no $\beta$ hydrogen), showing no 4,3 (or 1,2) structures, despite the fact that the in-chain units contain approximately 10% 3,4 structures. Similarly, the spectrum of the poly(2,3-dimethylbutadiene) chain end confirms the peak assignments based on the butadiene and isoprene studies, and shows an exclusively 1,4 structure, despite the presence of 15–20% 1,2 in-chain units. Hence, as in the case of the butadiene, it is suggested that these 1,2 or 3,4 units result from the presence of an undetectably small proportion of $\pi$-allyl chain ends in equilibrium with the main component of $\sigma$-bonded (localized) chain ends. The isoprene chain-end spectrum permits the resolution of cis- and trans-4,1 chain-end units, which are present in approximately the same ratio as their in-chain counterparts (cis/trans = 2). The observed differential rates of decomposition of these two isomeric forms of the chain end is taken as evidence that the 2,3 bond is not labile, *i.e.*, no 4,1–4,3 tautomerism. This further strengthens the hypothesis of a localized-delocalized equilibrium ($\sigma$-allyl–$\pi$-allyl) to account for the 3,4 unit content of the polymer, since such an equilibrium would not affect the cis–trans isomerism.

## Experimental Procedures

The general experimental procedures have already been described.[1] The only additional solvent used was cyclohexane-$d_{12}$ and this was obtained from Merck, Sharp and Dohme (98% minimum isotopic purity) and purified as described before.[1] The isoprene was Phillips 99% grade, while the 2,3-dimethylbutadiene was obtained from Chem Samples Co., and both were purified as described previously.[1] The *sec*-butyllithium was obtained in a *n*-hexane solution (1.5 $M$) from Foote Mineral Co. and was treated as described[1] for *n*-butyllithium. The isopropyllithium-$d_7$ was prepared as described below.

**Preparation of Isooropyllithium-$d_7$.** This was prepared from isopropyl-$d_7$ bromide (Merck, Sharp and Dohme) and lithium dispersion in *n*-hexane under high vacuum conditions. The procedure used was similar to that used[1] to prepare ethyllithium-$d_5$. The isopropyllithium-$d_7$ solution was filtered through a fine glass frit before being split down into initiator ampoules as described previously.[1] Titration of an initiator ampoule indicated that the yield of the reaction was about 65%, based on isopropyl-$d_7$ bromide.

## Results and Discussion

**Complexation with Monomer.** As in the case of butadiene described in the previous paper of this series,[1] a study was made of the nmr spectrum of the monomer in the presence of high concentrations of dienyllithium. As before, there was no noticeable effect of the presence of the isoprenyllithium on the isoprene spectrum. Again the conclusion must be made that, if there is any activated complex intermediate between the monomer and the growing chain end, then it can only be present in undetectably low concentrations, below 1%.

**Assignment of Chain-End Peaks for Isoprene.** The poly(isoprenyl)lithium chain ends provide a better nmr spectrum for analysis than the butadiene case, since the substitution of the methyl group for the vinylic hydrogen provides more detail. Figure 1i shows the 100-MHz spectrum of poly(isoprenyl)lithium prepared by reacting 0.4 $M$ isoprene with 0.2 $M$ perdeuteriobutadienyllithium "seed," while Figure 1ii shows the same material after pseudotermination with butadiene-$d_6$. From Figure 1ii (or from the in-chain peaks of Figure 1i), it is possible to compute a chain microstructure of 70% cis-1,4, 20% trans-1,4, and 10% 3,4. Unfortunately, slow initiation in this case led to an average of 8.8 isoprene units chain, thus decreasing the number of protonic chain ends, but the spectrum can still be clearly established. Thus the $\alpha$ protons again appear upfield but this time as a singlet. This absence of spin splitting can only be accounted for by absence of protons

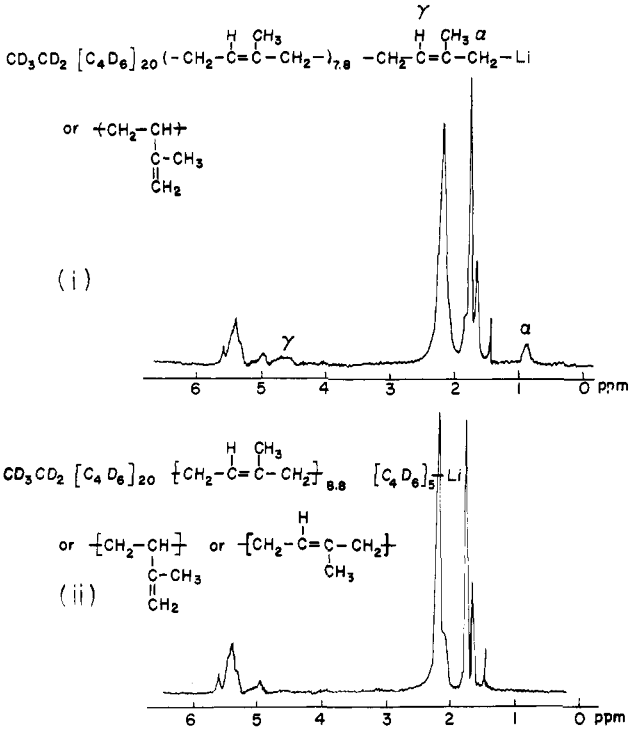


**Figure 1.** (i) Poly(isoprenyl)lithium in benzene-$d_6$ at 23° (100 MHz); (ii) same "pseudoterminated."

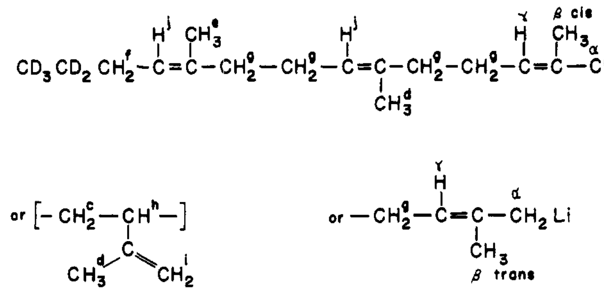
---

†Department of Chemistry, University of Stellenbosch, Stellenbosch, South Africa.

‡Bridgestone Tire Co., Tokyo, Japan.

§Kraftco, R&D Division, Glenview, Ill. 60025.

(1) M. Morton, R. D. Sanderson, and R. Sakata, *Macromolecules*, 6, 181 (1973).



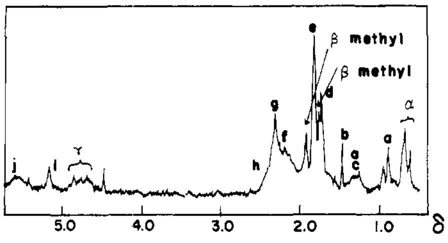


**Figure 2.** Spectrum of very low molecular weight poly(isoprenyl)-lithium in benzene-$d_6$ (100 MHz). (a) $n$-Hexane impurity; (b) cyclohexane, internal reference.

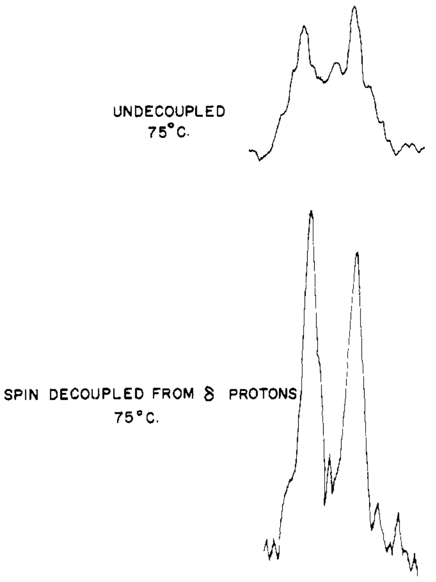


**Figure 3.** Spin decoupling of $\gamma$ absorption of poly(isoprenyl)lithium.

at the $\beta$ position, *i.e.*, if the methyl group is there instead. Hence one is led to conclude that this is the result of a *4,1-addition reaction.* This is further substantiated by the absence of any $\gamma$ peak in this spectrum, the $\beta$ peak appearing in its expected position. Using a time-average computer, it was possible to establish the absence of the $\beta$ peak down to less than 1% of the $\gamma$ peak area. As in the case of butadiene,[1] the $\delta$ peak was maked by the resonance of the in-chain methylenes at about 2.2 ppm.

There are two overlapping absorptions in the region of cis and trans allylic methyl protons. A better resolution of these peak identities was possible in the case of a lower molecular weight analog prepared by reacting 0.125 $M$ isoprene with 0.5 $M$ ethyllithium-$d_5$ instead of the butadienyl seed, and this is shown in Figure 2. In this case, with a higher concentration of chain ends, it can be seen that the $\beta$-methyl proton oeaks have separated from the in-chain methyl protons, and can be clearly seen, presumably as cis and trans peaks. The upfield peak appears between the in-chain cis-1,4 methyl and the in-chain combined trans-1,4 and -3,4 methyl peaks.

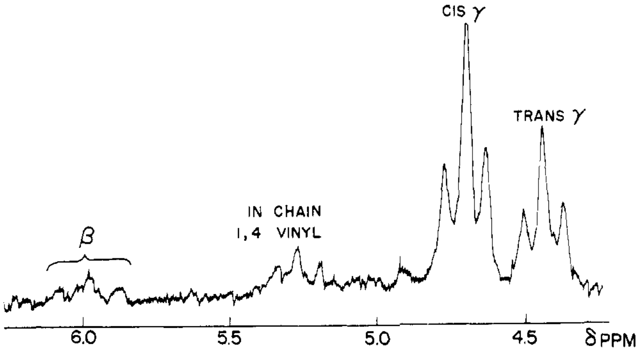


**Figure 4.** $\beta$ and $\gamma$ absorption area of 100-MHz spectrum of oligo(isoprenyl)lithium (initiated with *sec*-butyllithium in toluene-$d_8$).

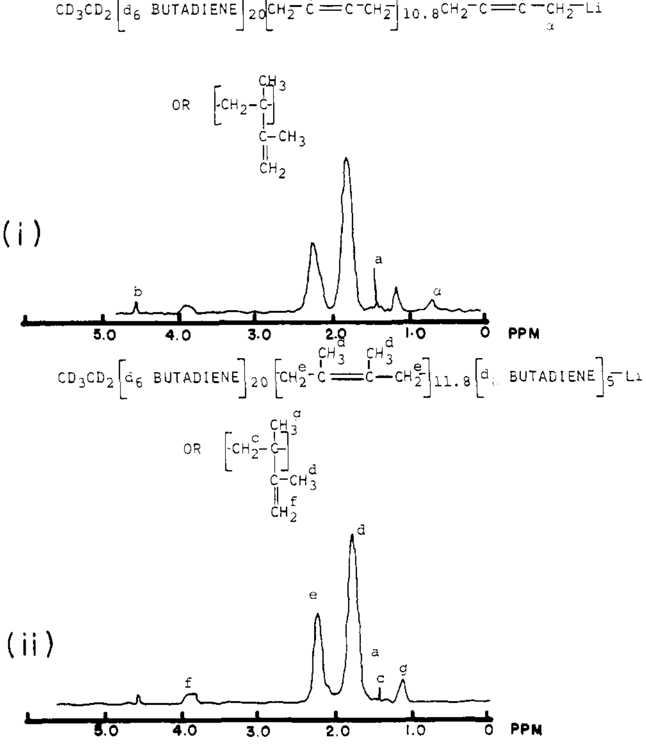


**Figure 5.** (i) Poly(2,3-dimethylbutadienyl)lithium in benzene-$d_6$ at 23° (100 MHz); (ii) same "pseudoterminated": (a) cyclohexane, internal reference; (b) nondeuteration in butadiene-$d_6$.

The separate cis and trans forms of the 4,1 chain end are also reflected in the $\gamma$ absorptions. Decoupling the $\gamma$ absorptions from the $\delta$, by irradiation at the resonance frequency of the latter, resolves the $\gamma$ protons into two individual peaks which can be clearly seen in Figure 3. An even better resolution of the cis and trans $\gamma$ proton absorptions was obtained on isoprenyllithium chain ends prepared by reacting 0.5 $M$ quantities of isoprene and sec-butyllithium in toluene-$d_8$. The latter initiator is known to have a very fast initiation rate,[2] relative to propagation, so that a 1:1 adduct should result, *i.e.*, no in-chain units of isoprene. This is shown in Figure 4, where the cis and trans $\gamma$ triplets are uncomplicated by their analogous in-chain absorptions.

Figure 4 also shows one additional and unexpected feature, *i.e.*, the appearance of a small $\beta$ absorption which represents about 9% of 1,4 chain-end units (rather than the expected 100% 4,1). Presumably the addition of the

---

(2) H. Hsieh, *J. Polym. Sci., Part A*, **3**, 163 (1965).

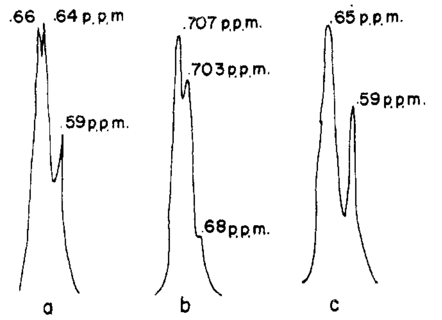


**Figure 6.** Poly(isoprenyl)lithium $\alpha$ peaks (100 MHz, benzene-$d_6$): (a) isoprenyllithium-ethyllithium-$d_5$ (1:9) at an early stage of reaction to lead to the final spectrum given in b; (b) isoprenyllithium-ethyllithium-$d_5$ (2:3); (c) isoprenyllithium-ethyllithium-$d_5$ (1:9).

highly reactive *sec*-butyllithium to isoprene is somewhat indiscriminate in this regard.

**Assignment of Chain-End Peaks for 2,3-Dimethylbutadiene.** A poly(2,3-dimethylbutadienyl)lithium prepared in 96% benzene-$d_6$ from 0.2 *M* poly(perdeuteriobutadienyl)lithium and 0.4 *M* dimethylbutadiene gave the spectrum shown in Figure 5i, while the "pseudoterminated" analog is shown in Figure 5ii. The resolution of fine details is hampered by the high ratio of protonic in-chain to chain-end units caused by the relatively slow rate of initiation compared to propagation of the dimethylbutadiene. The microstructure of the in-chain units was, as anticipated,[3,4] 80–85% 1,4 and 15–20% 1,2.

The obvious difference between this monomer system and those involving butadiene and isoprene, is the lack of both $\beta$ and $\gamma$ absorptions. Thus only an $\alpha$ peak is observed. A time-average computer was used to scan the $\beta$ and $\gamma$ resonance areas, but even though the sensitivity was better than ½% of the $\alpha$ peak, no $\beta$ or $\gamma$ peaks were observed. There was, once again, no evidence for 1,2 chain-end structures. The 1,4 localized chain end is therefore again the predominant species present, probably in equilibrium with $\pi$-allyllithium structure.

**Mechanistic Interpretations.** From the foregoing it can be concluded that the structure of the isoprenyllithium chain end is similar in nature to that of the butadienyllithium described in the previous publication,[1] *i.e.*, involving a covalent carbon–lithium bond and a 4,1 configuration, with no sign of any 1,2 or 4,3 nor of any $\pi$-allyl bonding, within the accuracy of the measurements.

As in the case of the butadiene,[1] a mechanism must be proposed for the formation of the 10% 3,4 in-chain structure from the exclusively 4,1 chain end units observed. Two such mechanisms can be proposed, both based on a dynamic equilibrium between the convalent 4,1 chain end and another type of chain end present in a concentration *too low to detect*. These possible equilibria can be expressed as shown in Charts I and II. Either of these equilibria could explain the formation of the observed 10% of 3,4 in-chain units, on the basis that the chain-end unit assumes its final configuration *at the time of reaction with the next monomer molecule*. This would require that, in the 4,1–4,3 tautomeric system, the 4,3 chain ends, which are too few to be observed, exhibit a much higher reactivity with monomer to account for as much as 10% in-chain structure. As for the covalent–$\pi$-allyl equilibrium, the same reasoning could be used, on the assumption that the $\pi$-allyl form can lead to *either 1,4 or 3,4 in-chain units*.

**Chart I**
**4,1–4,3 Tautomerism**

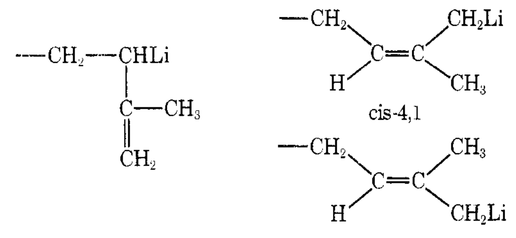
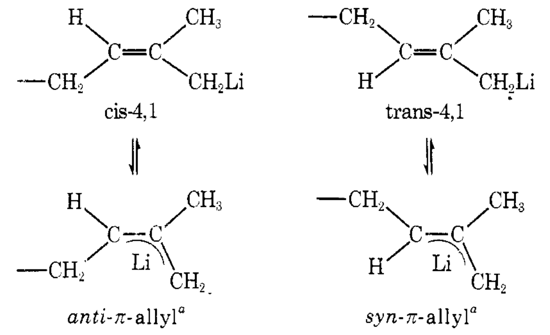


**Chart II**
**Covalent–$\pi$-Allyl Equilibrium**



[a] Terms assigned with reference to positions of $\gamma$ protons and lithium.

It is obvious, however, that the above two mechanisms would operate differently in that any *4,1–4,3 equilibrium would also involve a cis-4,1–trans-4,1 equilibrium*, whereas no such equilibration would result from the covalent–$\pi$-allyl system. It is possible to check the presence of any such equilibrium, and some experimental results bearing on this are shown in Table I, which shows the change in cis:trans ratio of isoprenyllithium $\gamma$ protons during "aging," *i.e.*, slow decomposition of the chain ends with time at 50°. It can be seen that this ratio changes, presumably due to a differential rate of destruction of the isomeric chain ends by side reactions.

The gradually changing cis:trans ratio as decomposition of chain ends proceeds precludes the existence of any real equilibrium by isomerization.[5a] Although this ratio seems to level off after several days, this happens only when the decomposition has led to some precipitation, and nmr readings become dubious. It is also interesting to note that the chain ends initiated by the isopropyllithium show a *decrease* in cis:trans ratio on aging, unlike the increase shown by the *sec*-butyllithium-initiated chain ends. Apparently the relative rates of decomposition of the chain ends is influenced by the initiator, which is of course always present in excess in these systems and is "cross-associated" with the chain ends.[6]

In view of the above evidence, it would appear that the 3,4 in-chain microstructure of polyisoprene is most reasonably accounted for on the basis of a covalent–$\pi$-allyl equilibrium, where the $\pi$-allyl form of the chain end can result in a 3,4 in-chain unit if the next monomer addition occurs at the 3 position. Hence the chain-end structure becomes an in-chain structure only after insertion of the following monomer unit.

---

(3) F. Schue, *Bull. Chim. Soc.*, 980 (1965).

(4) R. S. Stearns, U. S. Patent 483,147,242, Jan 19, 1964.

(5) (a) This conclusion is at variance with that of Schue, Worsfold, and Bywater,[5b] who claim to observe an isomerization equilibrium, based on observed changes in the spectrum with temperature. (b) F. Schue, D. J. Worsfold, and S. Bywater, *Macromolecules*, **3**, 509 (1070).

(6) M. Morton, R. A. Pett and L. J. Fetters, *Macromolecules*, **3**, 333 (1970).

**Table I**
**Aging of Oligo(isoprenyllithium) in Benzene-$d_6$ at 50°**

| Initiator | *sec*-$C_4H_9Li$ | *sec*-$C_4H_9Li$ | *i*-$C_3D_7Li$ |
|---|---|---|---|
| Chain Length | 1.23 | 2.70 | 1.32 |
| Time (Days) | Cis: Trans Ratio (γ H) | | |
| 0 | 1.6 | 1.7 | 1.8 |
| 3 | 1.9 | 2.4 | 1.3 |
| 5 | 2.3 | 2.3 | |
| 10 | 2.3 | 2.5[a] | |
| 11 | | | 1.1[b] |

[a] 45% of chain ends decomposed. [b] 26% of chain ends decomposed.

Several other features of the nmr spectrum of the isoprenyllithium deserve mention. The spectra shown heretofore were in benzene-$d_6$ solution. Changing the solvent to cyclohexane-$d_{12}$ yielded similar results for ethyllithium-$d_5$ initiation, except that the concentration of chain ends was lower due to a somewhat slower initiation rate. Using *sec*-butyllithium as initiator in cyclohexane-$d_{12}$ led to a faster initiation and hence to a higher chain-end concentration, so that the γ absorptions became clearer and could be seen as two overlapping triplets (cis and trans). From these spectra it appears that the cis and trans γ protons show a greater separation as the solvents change from cyclohexane to benzene to toluene. These changes can be ascribed to changes in solvent shielding effects and not to changes in electron density or structure at the γ position.

Another notable aspect of these spectra concerns the α-proton absorptions in the presence of excess ethyllithium-$d_5$. These have already been shown in Figure 2, but are shown more clearly in Figure 6, *i.e.*, the *multiple peaks*, which cannot be seen in the poly(isoprenyl)lithium initiated by the perdeuterobutadienyl seed (Figure 1). It seems reasonable to explain the multiple peaks, shown clearly in Figure 6, as due to cross-association complexes between the ethyllithium-$d_5$ and the oligo(isoprenyl)lithium, since they show a continuous change with extent of initiation. The rate of this interaggregate exchange must be sufficiently slow at room temperature, relative to the nmr time scale, to show the existence of separate species. This behavior is apparently different from that of the butadiene system, where interaggregate exchange is apparently rapid at all temperatures studied.

When the more reactive initiator isopropyllithium-$d_7$ was used to prepare an oligo(isoprenyl)lithium in benzene-$d_6$, the α absorption appeared as a single peak. Even when a 2:1 initiator to monomer ratio was used to ensure a large excess of initiator, the α resonance was still a single peak at room temperature. Thus, with isopropyllithium-$d_7$ there is either a rapid exchange between the different association complexes at room temperature or the chemical shifts produced in the different complexes are too small to be detected.

At 60°, the α resonance of the oligo(isoprenyl)lithiums prepared from isopropyllithium-$d_7$ was resolved into two peaks on the nmr spectrum. The two peaks had the same area ratio as the cis and trans γ-hydrogen peaks, so that they probably represent the cis and trans forms of the chain end. The higher molecular weight poly(isoprenyl)lithiums prepared from either ethyllithium-$d_5$ or perdeuteriopoly(butadienyl)lithium seed did not show this separation even at higher temperatures. Apparently the short chain lengths (~1.2-1.3 units) and higher monodispersity of the oligo(isoprenyl)lithiums prepared with isopropyllithium-$d_7$ resulted in the α resonance being resolved into two peaks at higher temperatures.

One other noteworthy point about the α peaks in Figure 6 is their slight downfield shift as the reaction proceeds (6a *vs.* 6b), the "final" position presumably being at 0.87 ppm, as indicated in Figure 1, where a longer chain length is involved. When protonic ethyllithium was used as initiator instead of the deuterated variety, a similar downfield shift was noted for the methyl and methylene protons of the ethyl group, as the reaction proceeded. This occurred in the case of both isoprene and butadiene. However, the *methyl* protons experienced a much greater shift than the *methylene, i.e.*, 3 Hz *vs.* 1 Hz (isoprene) and 5 Hz *vs.* 1 Hz (butadiene). All of these minor shifts can perhaps best be ascribed to solvent shielding differences as the chain grows and surrounds the associated structures of the chain end and initiator.

Since the mechanism described above (covalent-π-allyl equilibrium) proposed that the in-chain unit structure is only decided at the time of reaction of the chain-end unit with the incoming monomer, it is interesting to compare the cis:trans ratio of the chain-end unit with that of the in-chain units. It is, of course, not justifiable to assume that the two must be identical, since the two isomeric 1,4 chain ends may exhibit different reactivities (or different covalent-π-allyl equilibria). However, using either Figure 2 or 4, it was possible to calculate the fraction of cis γ protons as 60-65% and the trans γ as 35-40%. This compares with in-chain values of 70% cis and 30% trans units. Hence the chain-end isomers are only slightly enriched in cis content (if at all) during the propagation step.

Finally, some comments can be made about the effect of chain length on the microstructure. Thus, for isoprene, the microstructure of the first in-chain unit is the same as that of subsequent units, whereas in butadiene, the first units show abnormally high 1,2 content. This is in all likelihood related to the behavior of the initiator-(chain-end) aggregate, which exhibits a relatively slow rate of interchange in the case of isoprene and a much faster one for butadiene.

**Acknowledgment.** We acknowledge the financial support, during the course of this research, of three of the authors, by the General Tire and Rubber Co. of Alron, Ohio (R. D. S. and L. A. F.), and the Bridgestone Tire and Rubber Co. of Japan (R. S.). We acknowledge the kind assistance of Mr. E. R. Santee in obtaining the 100-MHz data as well as in their interpretation.