Nuclear Magnetic Resonance Studies of the Propagating Chain End in the Organolithium Polymerization of Dienes. III. 1,3-Pentadienes and 2,4-Hexadiene

Maurice Morton* and L. A. Falvo†

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

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ABSTRACT: High-resolution nmr studies have been carried out on the propagating chain end in the organolithium polymerization of a series of terminally substituted 1,3-dienes, as follows: 1,3-pentadiene (cis and trans), 2,4-hexadiene (cis,cis; cis,trans, and trans,trans); 2-methyl-1-*trans*-3-pentadiene, 3-methyl-1,3-pentadiene (cis and trans), and 4-methyl-1,3-pentadiene. All of the reactions were carried out in hydrocarbon solvents. The chain-end carbon atom was either primary or secondary, depending on the monomer, and sometimes on the initiator and chain length. Thus the 1,3-pentadiene exhibited both types of chain end (*i.e.*, both 1,4 and 4,1 addition) depending on conditions, the 2-methylpentadiene showed only primary chain ends (4,1 addition), while both the 3-methyl- and 4-methylpentadienes showed exclusively secondary chain ends (1,4 addition). The 2,4-hexadiene showed only secondary carbon–lithium, as expected. The interesting and unexpected finding was that the secondary carbon–lithium bonds found in these cases showed a *delocalized* structure, even in the hydrocarbon media used, unlike the localized σ bond found in the case of the primary carbon–lithium bonds.

The previous publications in this series[1,2] provided some insight into the structure of the propagating chain end in the organolithium polymerization of butadiene, isoprene, and 2,3-dimethylbutadiene in hydrocarbon media. The following terminally substituted 1,3-dienes have now been investigated by nmr techniques in a similar manner: 1,3-pentadiene (cis and trans), 2,4-hexadiene (cis,cis; cis,trans, and trans,trans), 2-methyl-1-*trans*-3-pentadiene, 3-methyl-1,3-pentadiene (cis and trans), and 4-methyl-1,3-pentadiene.

Experimental Procedures

High-vacuum techniques were used throughout for all monomer and solvent purifications. The basic procedures have been described elsewhere.[3] Purification of the solvents used (benzene-d_6, toluene-d_8, and cyclohexane-d_{12}) have been described in the previous papers.[1,2] Preparation and purification of ethyllithium-d_5, isopropyllithium-d_7, and *sec*-butyllithium have also been described previously.[1,2]

1,*cis*-3-Pentadiene, 1,*trans*-3-pentadiene, *cis,cis*-2,4-hexadiene, *cis,trans*-2,4-hexadiene, *trans,trans*-2,4-hexadiene, 2-methyl-1,*trans*-3-pentadiene, 3-methyl-1,*cis*-3-pentadiene, 3-methyl-1,*trans*-3-pentadiene and 4-methyl-1,3-pentadiene (Chemical Samples Co.) were degassed on the high-vacuum apparatus and distilled onto sodium mirrors. After contact with the sodium mirrors for a few hours, the monomers were distilled into storage ampoules and stored at −20°. Immediately before use they were distilled onto *n*-butyllithium and stirred for at least 30 min.

Initiator solutions of about 0.5 *M* concentration were prepared in nmr tubes as described previously,[1] and measured amounts of the monomers were distilled into the tubes. Generally, the molar ratios of monomer to initiator were in the range of 1–5, in order to produce short chain lengths.

Nuclear magnetic resonance spectra were recorded on either a Varian A-60 instrument (60 MHz) or a Varian HA-100 instrument (100 MHz). Chemical shifts values are reported in δ units, using tetramethylsilane as an internal reference standard.

Results and Discussion

1,3-Pentadiene. The reaction of 0.5 *M* 1,*trans*-3-pentadiene with 0.5 *M* ethyllithium-d_5 in toluene-d_8 resulted in an oligomer which gave the nmr spectrum shown in Figure 1. The chain length calculated, as usual, from the "active" *vs.* the in-chain peaks was about three units, so that about 66% of the ethyllithium-d_5 remained unreacted. The microstructure of the in-chain units was computed to be 80–85% 1,4 and 15–20% 1,2 while no 3,4 structure was detected. These values are similar to those reported by Schue.[4]

The chain-end unit was assigned a 4,1 structure as shown in Figure 1, based on the peak assignments as described below. The α resonance pattern was shown to be frequency dependent by a comparison of the 100- and 60-MHz spectra. Hence, the α resonance is apparently the sum of two unequally sized doublets which may be ascribed either to the cis and trans forms of the chain end or to different association structures of the chain end. Further confirmation of their doublet character was obtained by spin decoupling the α protons from the β protons, which resulted in the α resonance becoming an unsymmetrical singlet due to the overlap of two singlets. This splitting pattern also shows that the α protons are equivalent, *i.e.*, there is rotation about the α,β carbon–carbon bond, indicating a σ bond.

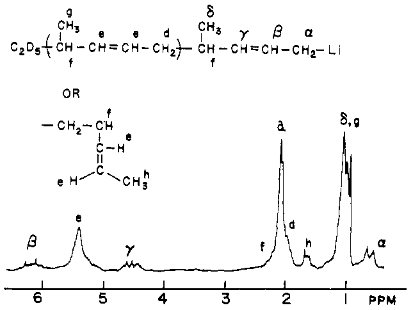

Figure 1. 100-MHz nmr spectrum of poly(1,3-pentadienyl)lithium in toluene-d_8. (a) Nondeuteration in toluene-d_8.

The γ absorption, centered at about 4.6 ppm, apparently consists of four peaks, which result from coupling with both the β proton and the single δ proton. Spin decoupling of the γ proton from the δ proton, as shown in Figure 2, gave a value of 17.0 cps for the γ,β coupling constant. This large coupling constant is, as usual,[5] best assigned to the trans chain end. This predominance of the trans 4,1 chain end correlates with the high in-chain trans-1,4 mi-

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

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

(2) M. Morton, R. D. Sanderson, R. Sakata, and L. A. Falvo, *Macromolecules,* **6,** 186 (1973).

(3) L. J. Fetters, *J. Res. Nat. Bur. Stand., Sect. A,* **70,** 421 (1966).

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

(5) L. M. Jackman and S. Sternhall, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Oxford Pergamon Press, New York, N. Y., 1969, pp 301 and 302.

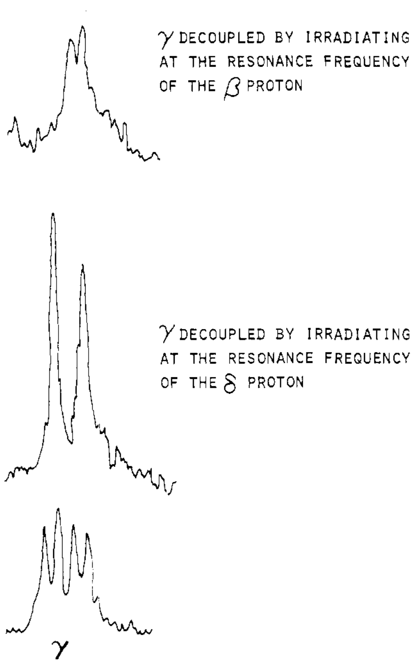

Figure 2. Decoupled γ resonance peaks.

crostructure reported for this polymer.[6,7] The γ resonance was also decoupled from the β resonance (Figure 2), further confirming the assignments of the active resonance peaks. It should be noted that the chain end is not solely trans, as the four trans γ peaks apparently overlap small cis γ peaks.

This nmr spectrum, therefore, shows that the poly(1,3-pentadienyl)lithium prepared with ethyllithium-d_5 is predominantly a 4,1-chain-end structure with a covalent carbon-lithium bond. The covalent nature of the bond is shown by the fact that the α protons are equivalent. It is further confirmed by the fact that the γ-hydrogen resonance is shifted only slightly upfield from the resonance peak position of the in-chain olefinic protons, indicating only a slight increase, if any, in the electron charge density on the γ carbon. These two features shown in the nmr spectrum would be inconsistent with a delocalized or π-allylic type carbon-lithium bond. This predominantly covalent species in hydrocarbons is analogous to those found for butadiene[1] and isoprene[2] in hydrocarbon solvents.

When 1,*cis*-3-pentadiene was reacted with ethyllithium-d_5 in benzene-d_6, the ratio of initiation to propagation was much lower. As a result the concentration of active chain ends was less, and only the α resonance peak could be seen in the nmr spectrum, since it consists of two protons. From the α resonance peak it appears that, again, the chain end structure is a covalent 4,1 species as in the case of the trans isomer.

A surprising observation in these systems was the absence of any 3,4 in-chain microstructure. Apparently, the 4,1 chain end, unlike that of isoprene, produces only a 1,4 (or 4,1) microstructure. Another observed anomaly was the occurrence of 20% in-chain 1,2 units, even though the 1,4-chain end unit, which could lead to these structures, was not observed. Evidently, the 1,4-chain end is very reactive and in too low a concentration to be detected in this system.

The existence of a 1,4-chain end was actually demonstrated by preparing a poly(1,3-pentadienyl)lithium species using more reactive initiators, such as *sec*-butyllithium and isopropyllithium-d_7. Figure 3 shows the 100-MHz nmr spectrum of the poly(1,3-pentadienyl)lithium prepared from 0.5 *M* 1,*cis*-3-pentadiene and 0.5 *M* isopropyllithium-d_7. Also shown is the spectrum of the same species after pseudotermination[1] with butadiene-d_6. The average chain length of this species was 2.7 units. The peaks were assigned on the basis of comparison with other poly(dienyl)lithiums, area ratios, splitting patterns, pseudotermination results, and spin-decoupling experiments. As can be seen, the peaks assigned to the γ-, β-, and δ-proton resonances disappeared upon pseudotermination and the peak partially assigned to the α-methyl resonance diminished in relative size. The α protons would be expected to show a resonance peak at about 1.0 ppm, where it is masked by the protons of the in-chain methyls (*cf.* Figure 5). The areas of the γ and β resonances are equal and can be spin-decoupled from each other. The γ proton can also be decoupled from the δ proton. Thus, the peak assignments in Figure 3 are confirmed.

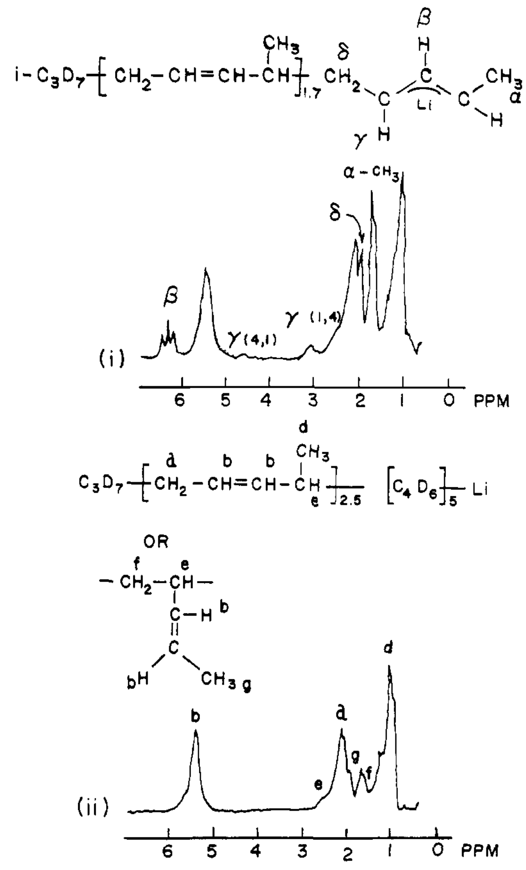

Figure 3. 100-MHz nmr spectra of 1,3-pentadienyllithium in benzene-d_6. (i) Before pseudotermination; (ii) after pseudotermination.

The spectrum shown in Figure 3 is interesting because it shows not only that the predominant chain-end structure is 1,4 but that it consists of a delocalized carbon-lithium bond, even in hydrocarbon solvents. This is in contrast to the results found[1,2,8] for isoprene and butadiene which showed predominantly covalent carbon-lithium species in hydrocarbons and predominantly delocalized species in polar solvents (ethers).

The fact that the chain end is 1,4 rather than 4,1 is clearly shown in the nmr spectrum. The presence of an active methyl resonance at 1.7 ppm shows that the methyl group is on the α carbon rather than the δ carbon. There

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

(7) G. Friedmann, *Bull. Chim. Soc.*, 2548 (1967).

(8) M. Morton, R. Sanderson, and R. Sakata, *J. Polym. Sci., Part B*, **9**, 61 (1971).

was no noticeable effect of the lithium on the methyl group of the 4,1 chain end produced from ethyllithium-d_5. The 1,4 structure of the chain end is further confirmed by the splitting pattern of the β-hydrogen resonance peak. It is a simple triplet, which, when spin decoupled from the γ hydrogen, formed a doublet. First-order nmr theory would predict such a splitting pattern for the β-hydrogen resonance of a 1,4 chain end but not for a 4,1 chain end. The β-hydrogen resonance peak of a 4,1 chain end is a more complex multiplet, as seen in Figure 1. Finally, the relative area of the resonance peak of the δ hydrogens indicates that it is due to two protons. Thus, the nmr evidence that the predominant chain end has a 1,4 structure is conclusive.

The fact that this chain end has a delocalized carbon-lithium bond is also very clear. As can be seen, the resonance peak of the γ hydrogen was shifted appreciably upfield from the resonance peak of the in-chain olefinic protons at 5.3 ppm and also from the resonance peak position (4.6 ppm) of the γ hydrogen of the covalent 4,1 chain end. In fact, the peak position of the γ hydrogen at 3.1 ppm is very close to that of the γ hydrogen of delocalized poly(butadienyl)lithium in H_4furan.[8] This large upfield shift is direct evidence of a high electron charge density on the γ carbon, thus indicating a delocalized, or π-allylic, carbon–lithium bond. Further evidence of the delocalized nature of the carbon–lithium bond is found in the downfield shift of the α-methyl resonance peak from the peak position of the in-chain methyl groups at around 1.1 ppm. Because of the electron charge on the α carbon, an upfield shift would normally be expected. The downfield shift is evidence of a change in hybridization of the α carbon from sp^3 to sp^2. Methyl groups attached to sp^2 hybridized carbons generally resonate downfield from methyl groups attached to sp^3 hybridized carbons. One final item of evidence for the delocalized nature of these species is the fact that these benzene-d_6 solutions were deep red in color. Benzene solutions of predominantly covalent poly(isoprenyl)lithium and poly(butadienyl)lithium at the same concentration exhibited only a pale yellow color.

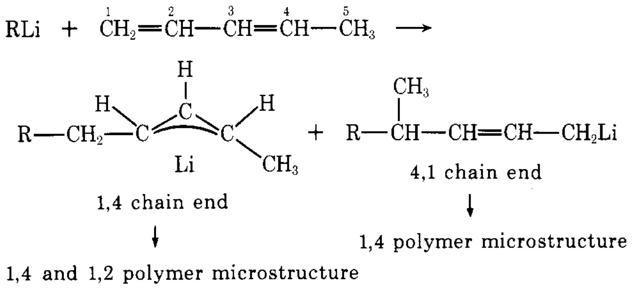
Hence there is conclusive evidence that, in the isopropyllithium-d_7-initiated system, poly(1,3-pentadienyl)lithium forms a predominantly 1,4 chain end. Furthermore, this chain end possesses a delocalized carbon–lithium bond even in hydrocarbon media. This is undoubtedly due to the fact that it is a secondary carbon–lithium bond. Apparently the less stable secondary bond is best stabilized through delocalization of the bonding electrons. The high concentration of 1,4 chain ends formed in this system, in comparison with the amount formed in the ethyllithium-d_5 system, is undoubtedly due to the greater reactivity of the secondary alkyllithium intiator used. When equimolar amounts of monomer and *sec*-butyllithium initiator were used, a delocalized 1,4 chain end was again formed. It was also found that the trans isomer of 1,3-pentadiene gave similar results with either of the above secondary alkyllithium initiators. However, in contrast with the ethyllithium-d_5-initiated system, the trans isomer had a slightly lower initiation to propagation ratio than the cis isomer.

It should also be pointed out that the delocalized structure pictured in Figure 3 can exist in four different isomeric configurations, depending on the relative placements of the α and γ hydrogens. The broadness of the active resonance peaks on the nmr spectrum would seem to indicate that more than one isomer is present. However, it was not possible to determine which isomers were present in this system. For convenience only one isomer is pictured in Figure 3.

If the spectrum in Figure 3 is examined closely, a small resonance peak can be seen at 4.6 ppm. This is the γ-hydrogen resonance of a small amount of covalent 4,1 chain ends formed in this system. When the molar ratio of monomer to initiator was 5, the relative amount of covalent 4,1-chain ends observed in the spectrum increased appreciably. In fact, over 80% of the chain-end structure observed in the spectrum was the covalent 4,1-chain end. It should be pointed out that two factors determine the relative amounts of the different chain ends observed: (1) the relative amounts of attack on the 1 *vs.* 4 positions of the monomer, and (2) the relative reactivities of the two chain ends. The 1,4-chain end, being a secondary carbon–lithium bond, can be expected to be much more reactive than the primary 4,1-chain end. In fact, the amount of 1,2 in-chain microstructure is about the same in the oligomers prepared with ethyllithium-d_5 and isopropyllithium-d_7. This seems to indicate that even in the ethyllithium-d_5 system most of the propagation occurs *via* the 1,4-chain end. Consequently, it is not surprising that using a high monomer to initiator ratio produces mostly 4,1 chain ends in the nmr spectrum, since the latter are, of course, much less reactive than the 1,4 chain ends.

Thus, the organolithium polymerization of 1,3-pentadiene apparently occurs as summarized in Scheme I. Steric and inductive effects of the methyl group should favor attack at the 1 position. However, these effects can be counterbalanced by energetic factors, due to the greater instability of the secondary carbon–lithium bond formed. Hence, attack occurs at both the 1 and 4 carbons of the monomer.

Scheme I



The high charge density on the γ-carbon of the 1,4-chain ends explains the relatively high (compared to isoprene or butadiene) amount of 1,2 in-chain structure formed. It is somewhat surprising that no 3,4 polymer microstructure is formed from the (covalent) 4,1 chain ends, since the covalent poly(isoprenyl)lithium and poly(butadienyl)lithium do produce a small amount of side vinyl microstructure, presumably from a small amount of a delocalized species in equilibrium with the covalent species.[8] A possible explanation for the lack of such a structure in this system is that the bulky methyl group on the δ carbon prevents monomer attack on the γ carbon.

A further point of interest found in this study is the isomerization of the 3,4 double bond. When 1,*trans*-3-pentadiene was polymerized with ethyllithium-d_5, the double bond of the 1,2 in-chain microstructure was found to be about 25–35% cis. Similar results have been reported by other workers.[7,9] This can only be ascribed to isomerization occurring during the polymerization, since isomerization of the monomer itself is ruled out, as the methyl absorption expected for 1,*cis*-3-pentadiene at 1.56 ppm did

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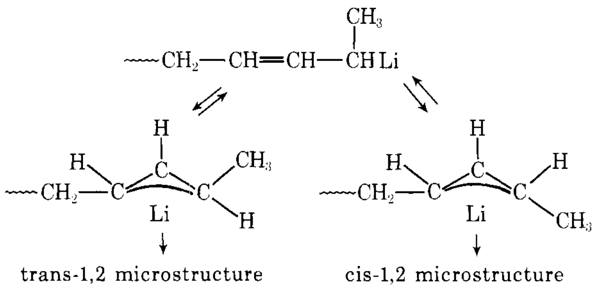
(9) J. Inomata, *Makromol. Chem.* 135, 113 (1970).

not appear as the reaction progressed. Thus, the best explanation for the isomerization is the proposed equilibrium between the delocalized species and covalent forms of the 1,4 chain end, the latter form being present in too low a concentration to be detected in the nmr spectrum. Such an equilibrium, as shown below, would allow rotation about the α,β carbon–carbon bond and would explain the isomerization (Scheme II). This isomerization strongly supports the theory previously proposed,[8] that, in the poly(butadienyl)lithium and poly(isoprenyl)lithium systems in hydrocarbon solvents, the covalent species observed in the nmr spectra are in equilibrium with an undetectable amount of delocalized species.

Scheme II



2,4-Hexadiene. 2,4-Hexadiene is an interesting diene monomer since it can react with an alkyllithium initiator to form only species possessing a secondary carbon–lithium bond. This monomer exists in three isomeric forms, cis,cis, cis,trans, and trans,trans. When mixed with equimolar amounts of ethyllithium-d_5 in toluene-d_8, only the trans,trans isomer was found to react at 23°, about 1 week being required for complete conversion. At 50° the other two isomers reacted in less than 1 week. However, because of an unfavorable initiation to propagation ratio, the nmr spectra of all three isomers showed no active resonance peaks due to the chain-end unit, only in-chain peaks being observed. The polymer spectra were interesting because they showed that the microstructure was entirely 2,5. No methyl resonance due to any 2,3 microstructure could be detected at 1.5–1.7 ppm. However, two doublets of different intensity from two different methyl groups could be observed around 1.0 ppm, but it could not be determined whether the two methyl groups represented cis and trans structures or isotactic and syndiotactic placements.

The 2,4-hexadiene isomers did react at 23° with both *sec*-butyllithium and isopropyllithium-d_7 in benzene-d_6 and produced nmr spectra that showed active resonance peaks of the end units. The trans,trans isomer had the best initiation to propagation ratio and reacted completely with an equimolar amount of initiator in less than 3 days. The other two isomers took over 1 week for complete reaction. Consequently, most of the study was carried out using the trans,trans isomer. All three isomers produced deep red solutions indicative of a delocalized species, and provided similar nmr spectra. Figure 4 shows the olefinic proton region of the 60-MHz nmr spectrum of the species produced from the reaction of 0.5 *M trans,trans*-2,4-hexadiene and 0.5 *M sec*-butyllithium in benzene-d_6. Also shown is the spectrum of the same species after pseudotermination[1] with butadiene-d_6. This poly(2,4-hexadienyl)lithium species had an average chain length of 2.2 units. The γ and β resonance peaks have an area ratio of one and they can be spin decoupled from each other. Of interest in this spectrum is the large upfield shift of the γ-hydrogen resonance peak from the in-chain olefinic proton peak at 5.2 ppm. As in the case of the 1,4 chain end of poly(1,3-pentadienyl)lithium, the peak position of 3.1 ppm is about the same as that of the γ-hydrogen peak position of delocalized poly(butadienyl)lithium in H_4furan.[8] Again, this large upfield shift is due to a high electron charge density on the γ carbon and is evidence of a delocalized or π-allylic carbon–lithium bond. This nmr evidence is in agreement with the deep red color of the solutions.

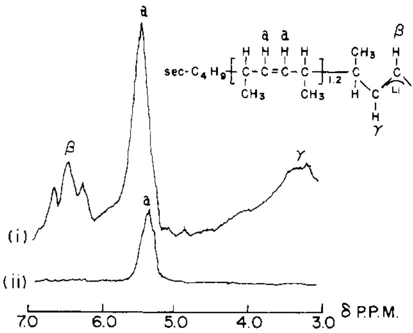


Figure 4. 60-MHz spectra of the olefinic protons of poly(2,4-hexadienyl)lithium in benzene-d_6 (Me_4Si internal reference). (i) Before pseudotermination; (ii) after pseudotermination.

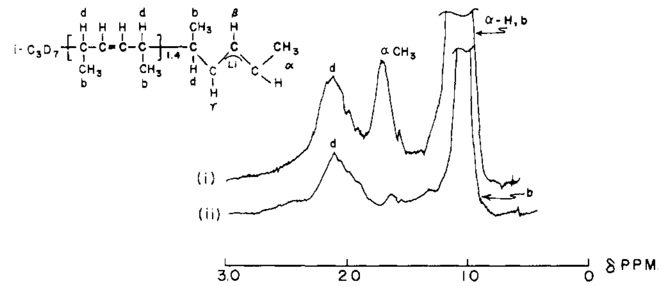


Figure 5. 100-MHz spectra of poly(2,4-hexadienyl)lithium in benzene-d_6. (i) "Living;" (ii) "pseudoterminated."

Further evidence of the delocalized nature of the carbon–lithium bond can be seen in the upfield portion of the nmr spectrum. Figure 5 shows the 100-MHz nmr spectrum of the methyl and methine protons of a species prepared using an isopropyllithium-d_7 initiator, and also the same species after pseudotermination. The peak assigned to the α methyl group has a 3 to 1 area ratio to either the γ- or β-hydrogen resonance peak. The α-hydrogen resonance is apparently masked by the large resonance peak of the in-chain methyl groups around 1.0 ppm. This would be expected from the known α resonance peak position of poly(butadienyl)lithium in H_4furan.[8] The downfield shift of the α methyl resonance peak is, as discussed previously, evidence that the α carbon is sp^2 hybridized. Thus the delocalized nature of the secondary carbon–lithium bond, even in hydrocarbon media, is confirmed.

In order to record the nmr spectrum at lower temperatures, a poly(2,4-hexadienyl)lithium was prepared in toluene-d_8. At 23° the nmr spectrum was the same as the spectrum recorded in benzene-d_6. At lower temperatures the resonance peaks broadened appreciably and, hence, the spectra provided no useful information. When *trans,trans*-2,4-hexadiene reacted with *sec*-butyllithium in cyclohexane-d_{12}, the initiation to propagation ratio was too low for the active absorptions of the end units to be observed in the nmr spectrum. However, the solution was deep red indicating that the delocalized species was formed and was soluble in a nonaromatic hydrocarbon.

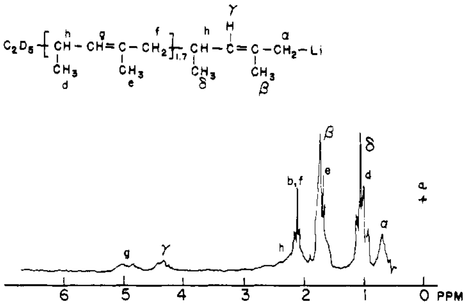


Figure 6. 100-MHz nmr spectrum of poly(2-methyl-1,3-pentadienyl)lithium in toluene-d_8. (a) Me_4Si, internal standard; (b) nondeuteration in toluene-d_8.

As can be seen in Figures 4 and 5 the active resonance peaks are relatively broad. Even at higher temperatures (60°) the resonance peaks remained broad. This broadness could be due to either viscosity effects or the presence of several isomers. A delocalized chain end as pictured in Figures 4 and 5 can actually exist as four different isomers, since both the α and γ hydrogens can be cis or trans to the β hydrogen. If the delocalized species is in equilibrium with a small amount of a covalent 2,5 species, the position of the α hydrogen would be independent of the isomeric configuration of the starting monomer. Since such an equilibrium apparently exists in the poly(1,3-pentadienyl)lithium system, it is most likely present in this system too. Thus, it is very possible that more than one isomer of the chain end is present in the 2,4-hexadiene case. However, it is not possible to determine how many isomers are present or their relative amounts.

The microstructure of the in-chain units of the oligomers prepared with the *sec*-alkyllithium initiators shows only 2,5 structures. This is in agreement with the microstructure of the poly-2,4-hexadiene prepared with ethyllithium-d_5. The delocalized nature of the chain-end makes this result somewhat surprising since the high electron charge density on the γ carbon would be expected to lead to some 2,3 addition. However, this situation is somewhat similar to the case of the pentadiene which also showed no 3,4 in-chain units. In both cases there is a methyl group on the δ carbon. This result reinforces the theory that a bulky substituent on the δ carbon will prevent attack on the γ carbon. Apparently, bulky substituents on the β carbon do not have the same effect since the 4,1 chain end of poly(isoprenyl)lithium produces 3,4 polymer microstructure.

The nmr spectra showed that these delocalized poly(2,4-hexadienyl)lithium species were stable in benzene-d_6 at 23° for several weeks.

The existence of these delocalized secondary carbon-lithium bonds in hydrocarbon media raises some interesting questions about association phenomena. It is known that organolithium compounds show various states of association in hydrocarbon media, but not in ethers (or other highly solvating solvents). It is also known that primary alkyllithiums are more highly associated than secondary alkyllithiums,[10] and that the primary carbon-lithium bonds obtained from butadiene and isoprene are associated in pairs[11] in hydrocarbon media where they exhibit a covalent bond, but are not associated in the presence of ethers, *e.g.*, H_4furan, where they have a delocalized structure. Hence the state of association of the above delocalized chain ends in hydrocarbon media is of great interest. Recent work[12] has in fact shown that the poly(hexadienyl)lithium chain ends are only slightly associated as dimers, the bulk of the species (~70%) being unassociated, presumably due to the delocalized (stabilized) character of the carbon-lithium bond.

2-Methyl-1,*trans*-3-pentadiene. The oligomer produced from the reaction of 0.5 *M* 2-methyl-1,*trans*-3-pentadiene and 0.5 *M* ethyllithium-d_5 in toluene-d_8 gave the nmr spectrum shown in Figure 6. The average chain length was 1.7 units, with about 40% of the initiator unreacted. The in-chain microstructure was unusual in that no 1,2 or 3,4 structures could be detected in the spectrum. This has also been reported by Cuzin *et al.*[13] who further defined the 1,4 units as 58–65% cis and 35–42% trans.

The assignment of the active resonance peaks from the end unit is again based on comparison with other poly(dienyl)lithiums, splitting patterns, area ratios, and spin-decoupling experiments. The spectrum in Figure 6 shows only α and γ absorption with no detectable β absorption. The observed chain end, therefore, must have resulted from a 4,1 addition with methyl substituents on the β and δ carbons. This is also confirmed by the fact that the α resonance is a singlet while the γ resonance consists of two overlapping doublets. Furthermore, the ratio of the α peak area to the γ peak area is 2, within an error of 2%.

In the 100-MHz spectrum (Figure 6) the γ doublets overlap to give three peaks, but in the 60-MHz spectrum the overlap is less severe, showing all four peaks. Both doublets can be spin decoupled from the δ proton. The downfield doublet is assigned to the cis chain end as in the isoprene study.[2] Area measurements show that, in this case, the cis:trans chain-end ratio is 66:34 and is in excellent agreement with the values of the 1,4 in-chain microstructure reported by Cuzin *et al.*[13]

As was also found in the butadiene[1] and isoprene[2] studies this poly(2-methyl-1,3-pentadienyl)lithium possesses a covalent carbon-lithium bond in hydrocarbon solvents. This is shown by the fact that the α protons are equivalent in the nmr spectrum indicating a rotation about the α,β carbon-carbon bond. Also the γ-hydrogen resonance is shifted only slightly upfield from the resonance peak position of the in-chain olefinic protons, which indicates only a slight increase, if any, in electron charge on the γ carbon. Thus, this chain-end structure is consistent with previous results[1,2,8] which showed that poly(dienyl)lithiums with primary carbon-lithium bonds form predominantly covalent species in hydrocarbon solvents.

When isopropyllithium-d_7 was used as an initiator, a spectrum similar to the one shown in Figure 6 was again produced, the only difference being a shorter average chain length of 1,4 units. Again no β-hydrogen resonance was detected. Thus it appears that with this monomer, unlike 1,3-pentadiene, all attack occurs at the 4 carbon. This result is not surprising since inductive effects of the methyl group on the 2 carbon would make the 1 carbon less reactive in comparison to that of the 1,3-pentadiene. Consequently, no 1,2 polymer microstructure is formed in these systems. The chain-end structure of poly(2-methyl-1,3-pentadienyl)lithium is very similar to that of poly(isoprenyl)lithium, but it does not produce any 3,4 polymer microstructure. Again this is best explained by steric effects of the bulky methyl group on the δ carbon.

3-Methyl-1,3-pentadiene and 4-Methyl-1,3-pentadiene. The monomer 3-methyl-1,*trans*-3-pentadiene was

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(10) T. L. Brown, *Advan. Organometal. Chem.*, 3, 365 (1965).

(11) M. Morton, L. J. Fetters, R. A. Pett, and J. F. Meier, *Macromolecules*, 3, 327 (1970).

(12) M. Morton, L. A. Falvo, and L. J. Fetters, *J. Polym. Sci., Part B*, 10, 561 (1972).

(13) D. Cuzin, Y. Chauvin, and G. Lefebvre, *Eur. Polym. J.*, 3, 581 (1967).

appreciably more reactive with ethyllithium-d_5 in toluene-d_8 than either 1,3-pentadiene or 2-methyl-1,3-pentadiene, the reaction at 23° being complete within 24 hr, compared to two or more days for the latter. However, no chain-end absorptions could be detected in the nmr spectrum because of an unfavorable initiation to propagation ratio. The microstructure of the polymer produced was 80 ± 5% 1,4 and 20 ± 5% 1,2. Using isopropyllithium-d_7 as an initiator in benzene-d_6 the reaction was complete in less than two hours and the solution had a deep red color, indicating a delocalized carbon–lithium bond. However, no absorptions from γ hydrogens could be seen in the nmr spectrum (there would be no β protons in a 1,4 chain end).

Furthermore, this spectrum contained a broad resonance peak from the in-chain units centered around 2.8 ppm. This peak could easily mask a small γ-hydrogen resonance peak. Upon pseudotermination of this species the ratio of the areas of the two methyl group resonance peaks at 1.6 and 1.1 ppm decreased from approximately 2.3 to 1.5. This shows that part of the resonance peak at 1.6 ppm was due to the α-methyl group of the 1,4 chain end. This result is analogous with that found for the 1,3-pentadiene (see Figure 3) and confirms the presence of the delocalized 1,4 chain end.

It is not surprising that the chain-end is exclusively 1,4 in the case of this monomer, since the inductive effect of the methyl group on the 3 carbon would make attack at the 1 carbon more favorable than in the 1,3-pentadiene case. The delocalized bond, with a high charge density on the γ carbon, explains the relatively high amount (~20%) of 1,2 microstructure formed in this polymerization in hydrocarbon media. Also the high amount of 1,2 microstructure indicates that methyl groups on the β carbon, unlike methyl groups on the δ carbon, do not prevent monomer attack at the γ carbon. The high reactivity of the secondary carbon–lithium bond also explains the high reactivity of this monomer compared to the other 1,3-pentadienes.

Another monomer studied was 4-methyl-1,3-pentadiene. The reaction of a 0.5 M solution of ethyllithium-d_5 in toluene-d_8 with an equimolar amount of monomer was very slow, with only 40–45% conversion after 11 days at 23°. Using *sec*-butyllithium as an initiator in benzene-d_6, the reaction was complete in 24 hr. However, in both cases no active absorptions from the chain end unit could be observed in the nmr spectrum because of an unfavorable initiation to propagation ratio. The solution of the *sec*-butyllithium initiated species had a deep red color, again indicating a delocalized carbon–lithium bond. It is very likely that steric and inductive effects of the two methyl groups on the 4 carbon cause exclusive attack on the 1 carbon. Such attack would produce a 1,4 chain end that would possess a tertiary carbon–lithium bond. The instability of such a bond again should lead to a delocalized species, even in hydrocarbons. Also such a species should be very reactive and would account for the high propagation to initiation ratio found for this monomer.

The microstructure of the poly(4-methyl-1,3-pentadiene) polymers formed was about 83% 1,4 and 17% 1,2. These results agree with those of Cuzin *et al.*[13] who further determined by ir that the 1,4 structure was all trans.

These results thus show that delocalized carbon–lithium bonds can exist in hydrocarbon media, and thus support the previously proposed theory that the 1,2 and 3,4 polymer microstructures formed in polybutadiene and polyisoprene, respectively, is due to a small, undetectable amount of delocalized chain ends in equilibrium with the covalent species detected in the nmr spectrum.

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Structure Analysis of Poly(propylene-α-d oxide) by High-Resolution Nuclear Magnetic Resonance Spectroscopy

Nobuki Oguni,* Shoji Watanabe, Motochika Maki, and Hisaya Tani*

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.

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ABSTRACT: Nmr spectra of poly(propylene-α-d oxide) prepared using several types of catalyst were taken and analyzed. Nmr spectra of methylene protons were resolved as dyads arising from the difference in steric environment in the contiguous two monomeric units. Nmr spectra in deuteriochloroform solution showed two pairs of quartets, one of which on downfield was assigned to the methylene protons of head-to-tail linkages, the other on upfield to tail-to-tail linkages. On the other hand, nmr spectra of methylene protons in benzene solution showed splitting into isotactic and syndiotactic dyads of absorption assigned to head-to-tail methylene protons. According to these assignments, microstructure of poly(propylene-α-d oxide) prepared with several types of catalyst could be determined.

Information concerning the microstructure of the polymer is an essential prerequisite for the elucidation of the polymerization mechanism and for the characterization of the polymer samples. The use of nmr spectra in the determination of the tacticity of vinyl polymers has been developed, but the application of this valuable technique to the polymer in which the repeating monomeric unit has three backbone atoms, has not been made so extensively. In a preliminary report,[1] we described the nmr analysis of poly(propylene-α-d oxide) briefly and more recently the nmr spectra of poly(propylene-α-d sulfide) were analyzed in terms of dyads of methylene protons.[2]

(1) H. Tani, N. Oguni, and S. Watanabe, *J. Polym. Sci., Part B*, 6, 577 (1968).

(2) K. J. Ivin and M. Navratil, *J. Polym. Sci., Part B*, 8, 51 (1970).