1 and 7. This ratio is also given in Table III. It is interesting to note that the correspondence is rather good between the values of these ratios.

As is already mentioned, the steady state was assumed in the above statistical analysis of the monomer sequence distribution. We should, however, bear in mind that the validity of this treatment is limited because of the low molecular weights of the present copolymers. The preliminary result of the application of the statistical analysis for finite chain[16] showed that in the present system the statistical analysis for infinite chain is applicable approximately to the copolymers having the molecular weights larger than 2500.

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NMR Studies of Polymerization of 1,3-Dienes with Bis(π-crotylnickel iodide)

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ABSTRACT: High-resolution NMR studies have been made of the polymerization of 1,3-dienes with bis(π-crotylnickel iodide). The observed proton resonances of the reaction products of this complex with butadiene, isoprene, 2-ethyl-, 2-isopropyl-, and 2-*tert*-butylbutadienes, 2,3-dimethylbutadiene, 1,3-pentadienes, and 4-methyl-1,3-pentadiene indicate that the end unit of the propagating polymer chain is of π-allylic structure. The type of an alkyl substituent greatly influences the relative content of syn and anti isomers in these adducts.

It can be said without exaggeration that NMR spectroscopy contributed much to the progress of π-allylic compound chemistry, for it made possible a more penetrating insight into the nature of metal–carbon bonds. Successful application of NMR spectroscopy was reported in a series of papers on polymerization of 1,3-dienes using organic compounds of lithium,[1–8] palladium,[9–13] and nickel[14–24] published almost simultaneously.

In the present paper, the results of NMR studies on the reactions of 1,3-dienes of various structure with bis(π-crotylnickel iodide) and its deuterated analogues which were carried out in our laboratory are summarized. To our mind, these studies have revealed some fundamental trends in the coordination polymerization which can contribute first of all to a better understanding of stereocontrol phenomena.

Experimental Section

Perdeuteriobutadiene was prepared from hexachlorobutadiene[25] and 1,1,4,4-tetradeuteriobutadiene was prepared by thermal decomposition of 2,5-dihydrothiophene-*2,2,5,5*-d_4 dioxide.[26] Similarly 1,1,4,4-tetradeuterioisoprene was prepared from isoprene-d_4 sulfone.[3] Complexes $(C_4H_7NiI)_2$, $(C_4D_5H_2NiI)_2$, and $(C_4D_7NiI)_2$ were synthesized from corresponding crotyl iodide and carbonylnickel.[27] All hydrocarbons used were dried over calcium hydride.

The reactions of 1,3-dienes with π-crotylnickel complexes in benzene solution were carried out under argon in glass vessels fitted with baffle-boards. 1,3-Diene was charged into the upper part of the vessel, with the lower part being filled with the complex solution containing a small amount of tetramethylsilane used as an internal standard for NMR measurements.

NMR spectra were recorded using a Jeol Co. JNM + 3H-60 NMR spectrometer and a Bruker HX-90 spectrometer.

Results and Discussion

Reaction with Butadiene. NMR spectra of the reaction mixtures indicated that, first, the addition of bis(π-crotylnickel iodide) to butadiene is a relatively slow process which allows a clear-cut differentiation of the reaction by separate stages to be made; second, all the molecules of the crotyl complex are involved in the reaction; and, third, after each act of insertion the π-allylic bond is regenerated in the adducts.

The ^1H NMR spectrum of bis(π-crotylnickel iodide) (Figure 1) shows five resonances: three doublets at τ 7.01 (H^b), 8.50 (H^c), and 8.86 (syn-CH_3), and two multiplets at τ 5.32 (H^a) and 7.30 (H^d). In the presence of perdeuteriobutadiene a gradual weakening of these signals is observed and new signals at τ 7.95, 8.38, and 4.55 (Figure 2) appear which characterize protons of the crotyl group separated from the metal. After a definite period of time a full disappearance of the initial complex resonances is observed. The change of signal intensities in this reaction provides information on the insertion of the first butadiene molecules.

It should be noted, however, that in the spectrum of a reaction mixture consisting of the perdeuterated complex and butadiene (Figure 3) the signals of a substituted π-crotyl ligand appear: the protons H^a (τ 5.30), H^b (τ 7.02), H^c (τ 8.50), H^d (τ 7.30), and the methylene group protons in α-position to the allylic carbon atom (τ 8.37). The insertion of the second and other diene molecules does not lead to any change in these signal intensities and results in the appearance of methylene (τ 7.95) and methine (τ 4.55) proton resonances in the spectrum.

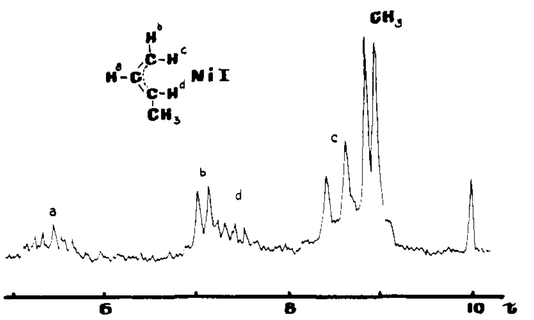


Figure 1. NMR spectrum (60-MHz) of bis(π-crotylnickel iodide).

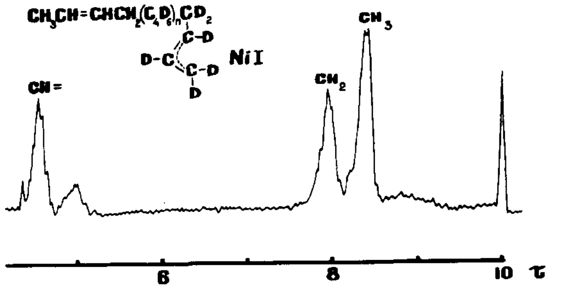


Figure 2. NMR spectrum (60-MHz) of a reaction mixture $(C_4H_7NiI)_2$ and C_4D_6 8.5 h after the beginning of a reaction; temperature, 25 °C. Initial concentration: $[C_4H_7NiI] = 0.46$ M, $[C_4D_6] = 5.0$ M.

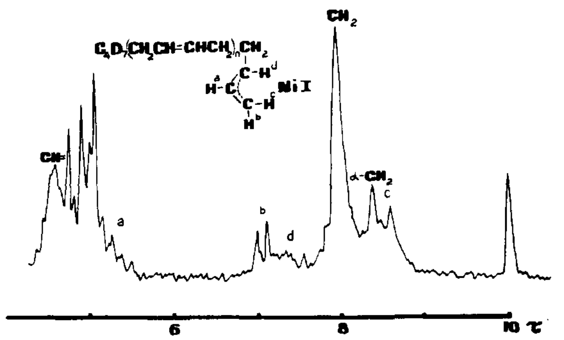


Figure 3. NMR spectrum (60-MHz) of a reaction mixture $(C_4D_7NiI)_2$ and C_4H_6 (10 h, 25 °C). Initial concentrations: $[C_4D_7NiI] = 0.70$ M, $[C_4H_6] = 2.7$ M.

The multiplet character of signals from H^d-type protons of bis(π-crotylnickel iodide) and of the above mentioned adducts makes it difficult to determine unequivocally the π-allylic ligand geometric configuration. A more reliable determination of an adduct structure was carried out by studying the NMR spectra of the reaction products of a complex and a diene, both containing protons at methine carbon atoms only.

In the spectrum of $(C_4D_5H_2NiI)_2$ there are but two doublets at τ 5.33 (H^a) and 7.34 (H^d) (Figure 4i). The spin–spin coupling constant $J_{ad} = 13$ Hz indicates that the π-crotyl ligand is of syn configuration. The addition of this complex to 1,1,4,4-tetradeuteriobutadiene does not in principle cause any change in the spectrum except that the signals from new allylic protons ($H^{a'}$ and $H^{d'}$) appear as doublets at τ 5.26 and 7.29 in a somewhat lower field (Figure 4ii and 4iii). New resonances at τ 4.5–4.6 are due to the methine protons of butadiene units in the polymer chain. From NMR spectra of the reaction mixtures $(C_4D_7NiI)_2 + C_4D_4H_2$, $(C_4D_5H_2NiI)_2 + C_4D_6$, and $(C_4D_5H_2NiI)_2 + C_4D_4H_2$ it was concluded that these signals are not equivalent because their chemical shifts differ from each other by 0.1 ppm. In the initial stages of the interaction the resonance in the high field is more intensive (τ 4.60). After the maximum signal intensity is attained it shows no tendency to increase or diminish (system $(C_4D_5H_2NiI)_2 + C_4D_6$). At the same time, the intensity of the resonance at τ 4.50 increases practically up to a complete consumption of the monomer ($C_4D_4H_2$). Signals which appear in the high field are assigned to the butadiene fragment attached to the end π-crotyl unit because they disappear when the active sites are deactivated by ethyl alcohol saturated with air. Spectra of deactivated macromolecules show a resonance only at τ 4.50 in the methine proton region. An upfield shift of the methine proton signals of the penultimate unit is indicative of its coordination with a transition metal, though this coordination is weak.

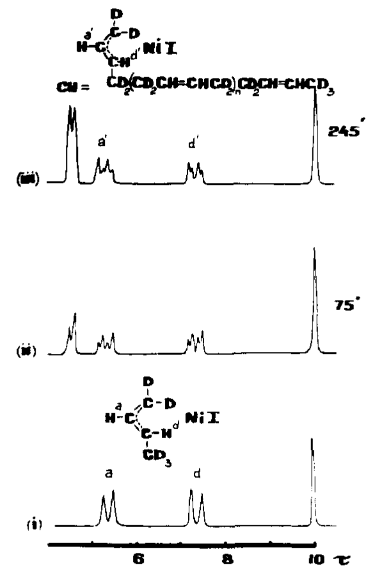
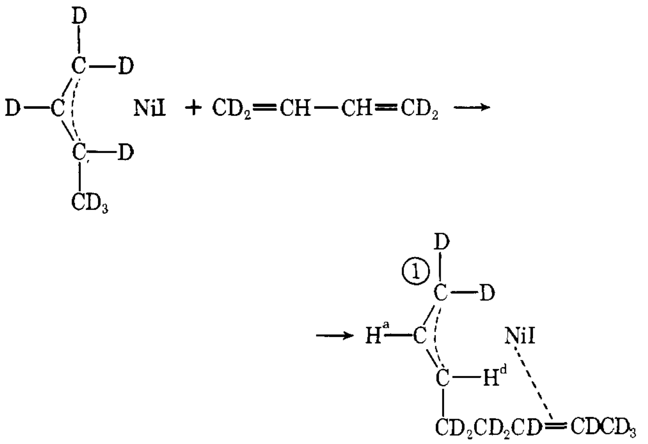


Figure 4. NMR spectra (60-MHz) of bis(π-crotyl-d_5-nickel iodide) and its reaction products with 1,1,4,4-tetradeuteriobutadiene. Initial concentrations: $[C_4D_5H_2NiI] = 0.47$ M, $[C_4D_4H_2] = 1.23$ M. Temperature, 25 °C.

Individual stages of the polymerization can be easily ascertained using system $(C_4D_7NiI)_2 + C_4D_4H_2$. The ^1H NMR spectrum of the initial complex naturally shows no signals. After the first diene molecules insertion there appear doublets from the allylic protons H^a (τ 5.23) and H^d (τ 7.29) (Figure 5):



where a figure inclosed in a circle denotes a serial number of the inserted butadiene-d_4 molecule.

The second monomer molecule insertion does not cause any change in the position and the intensity of signals from pro-

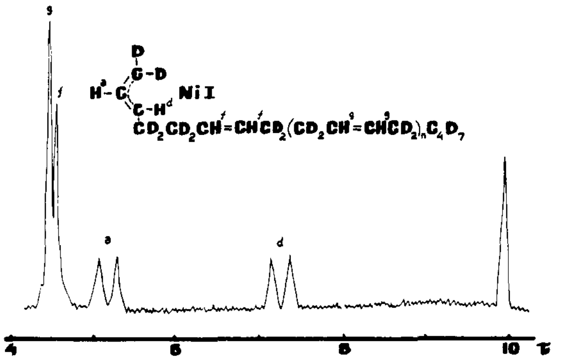
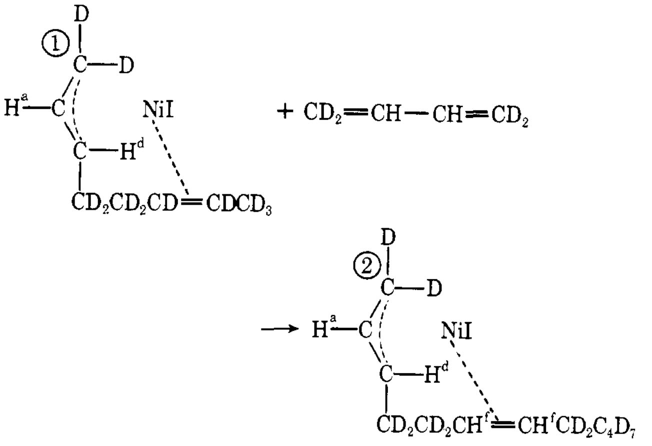
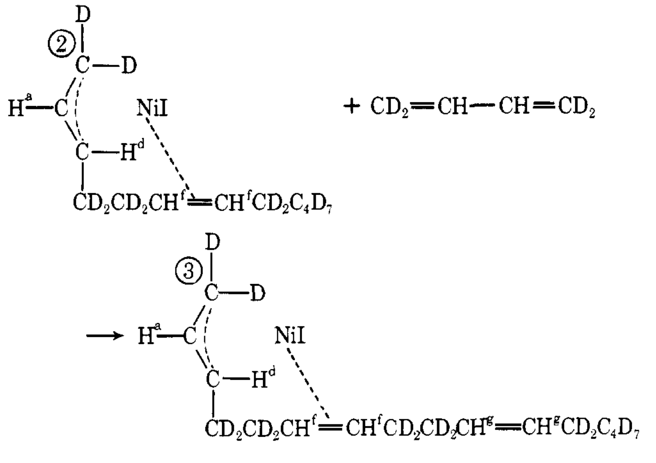


Figure 5. NMR spectrum (60-MHz) of the $(C_4D_7NiI)_2$ reaction product with 1,1,4,4-tetradeuteriobutadiene (190 min, 26 °C). Initial concentrations: $[C_4D_7NiI] = 0.36$ M, $[C_4D_4H_2] = 3.8$ M.

tons H^a and H^d. But in this case a displaced unit gives a signal at τ 4.60 (H^f):



The appearance of a signal at τ 4.50 (H^g) is indicative of the third butadiene-d_4 molecule insertion:

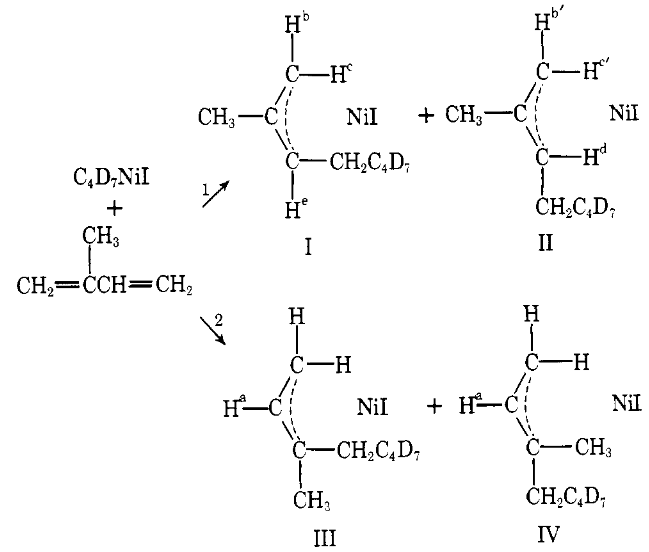


In the case of an adduct with three butadiene units the intensities of allylic protons ($H^a + H^d$), H^f, and H^g are equivalent. The insertion of the fourth and other butadiene molecules causes a further increase in the intensity of a signal at τ 4.50.

The spin–spin coupling constant $J_{ad} = 13$ Hz is found to remain unchanged in all the stages of the controlled insertion, which is indicative of syn configuration of the end unit. This agrees well with the trans-1,4 microstructure of macromolecule units formed in the presence of bis(π-crotylnickel iodide).

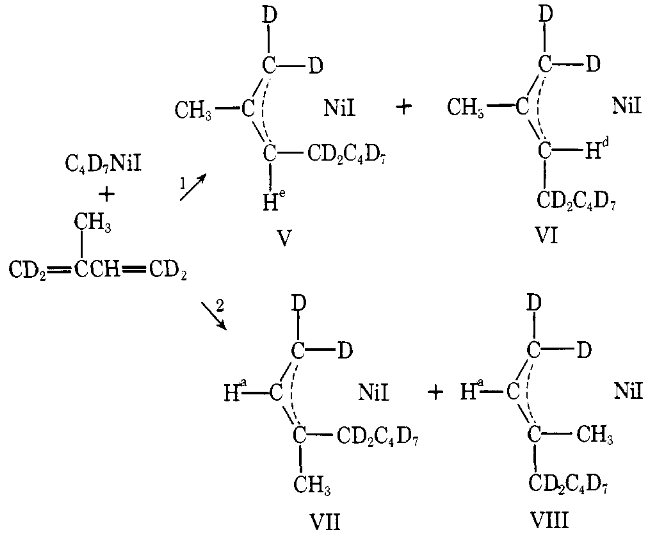
Reactions with Isoprene. Theoretically, the number of π-allylic 1:1 adducts of isoprene may be as great as four (Scheme I).

Scheme I



The NMR spectrum recorded some time after the beginning of the reaction between π-perdeuteriocrotylnickel iodide and isoprene indicated that all the four possible types of complexes are present in the reaction mixture (Figure 6). The most typical signals due to complexes I and II are singlets from H^b (τ 6.58) and $H^{b'}$ (τ 6.75) protons, and those due to complexes III and IV are singlets from the *syn*- and *anti*-methyl groups at τ 8.60 and 9.17, respectively. The quantitative ratio of the above mentioned structures was determined using the system $(C_4D_7NiI)_2$ + 1,1,4,4-tetradeuterioisoprene. The spectrum of this mixture is simpler due to the absence of signals from all the methylene protons, with all other resonances being singlets (Figure 7). The four types of structures (V–VIII) present in the solution 260 min after the beginning of the reaction between the complex and diene (Scheme II) were assigned according to the following signals: τ 5.9 (H^e, V), τ 7.05 (H^d, VI), τ 5.46 and 8.60 (H^a and *syn*-CH_3, VII), τ 5.39 and 9.17 ($H^{a'}$ and *anti*-CH_3, VIII). The NMR characteristics of I–VIII adducts are given in Table I.

Scheme II



From the ratio of the sums of signal integral intensities ($H^a + H^{a'}$)/($H^d + H^e$) (Figure 7) the contribution of reaction paths 1 and 2 can be evaluated (Schemes I and II); the addition of

Table I
Chemical Shifts of Protons in 1:1 Adducts of C_4D_7NiI and Isoprene or Isoprene-d_4

Complex	Chemical shifts of protons, τ values								
	H^b	$H^{b'}$	H^c	$H^{c'}$	H^e	H^d	CH_3	H^a	$H^{a'}$
I	6.58		7.62		5.9		8.40		
II		6.75		8.2		7.05	8.50		
III	[a]		[a]				8.60	[a]	
IV		[a]		[a]			9.17		[a]
V					5.9		8.38		
VI						7.05	8.48		
VII							8.60	5.46	
VIII							9.17		5.39

[a] No assignment due to overlapping by more intensive signals.

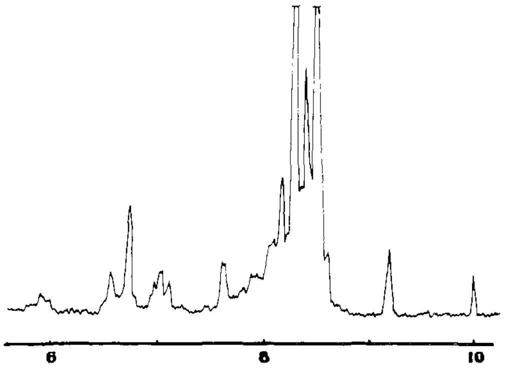


Figure 6. NMR spectrum (90-MHz) of a reaction mixture of $(C_4D_7NiI)_2$ and isoprene (100 min, 20 °C). Initial concentrations: $[C_4D_7NiI] = 1.17$ M, $[C_5H_8] = 0.83$ M.

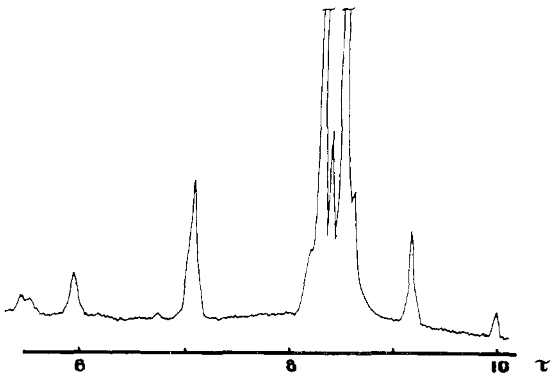


Figure 7. NMR spectrum (90-MHz) of a reaction mixture of $(C_4D_7NiI)_2$ and 1,1,4,4-tetradeuterioisoprene (260 min, 20 °C). Initial concentrations: $[C_4D_7NiI] = 1.02$ M, $[C_5D_4H_4] = 1.93$ M.

π-crotylnickel iodide to isoprene proceeds mainly (90%) with the formation of 1,2-disubstituted π-allylic complexes.

The ^1H NMR spectra show that the concentrations of syn- and anti-1,2-disubstituted π-allylic adducts change with time. During the first minutes of the reaction between $(C_4D_7NiI)_2$ and isoprene (Figure 8) two signals from H^b and H^e protons of anti complex I appear which are characterized by equivalent intensities: a singlet at τ 6.58 and a widened resonance at τ 5.9. Some time latter the syn isomer II is formed, as evidenced by signals from $H^{b'}$ and H^d protons: a singlet at τ 6.75 and a doublet of doublets at τ 7.05. Under experimental conditions given in Figure 8 complex I is formed more readily than complex II at the very beginning of the reaction. This can be easily seen from the kinetic curves of Figure 9. The shape of curves 1, 3, and 5 with a bend corresponding to a maximum concentration of the anti complex and the S form of curves 2, 4, and 6 showing the variation of syn complex concentration indicates that the latter is formed exclusively as a result of the anti complex isomerization. From Figure 9 it is also seen that a rise in the reaction temperature leads to a decrease in the proportion of anti-1,2-disubstituted π-allylic complexes.

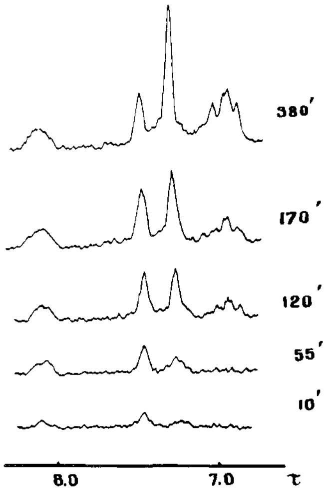


Figure 8. NMR spectra (90-MHz) of a reaction mixture of $(C_4D_7NiI)_2$ and isoprene. Initial concentrations: $[C_4D_7NiI] = 0.49$ M, $[C_5H_8] = 2.0$ M. Temperature, 16 °C.

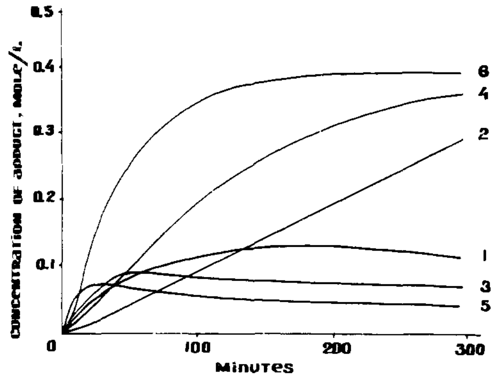


Figure 9. Kinetic curves of the formation of 1:1 anti-(1,3,5) and syn-(2,4,6) adducts of C_4D_7NiI and isoprene at temperatures: (1,2) 16 °C; (3,4) 26 °C; (5,6) 35 °C. Initial concentrations: $[C_4D_7NiI] = 0.49$ M, $[C_5H_8] = 2.0$ M.

Reactions with 2-Ethylbutadiene, 2-Isopropylbutadiene, and 2-*tert*-Butylbutadiene. The initial stage of the reaction between $(C_4D_7NiI)_2$ and 2-ethylbutadiene as compared to that of the reaction with isoprene is characterized by

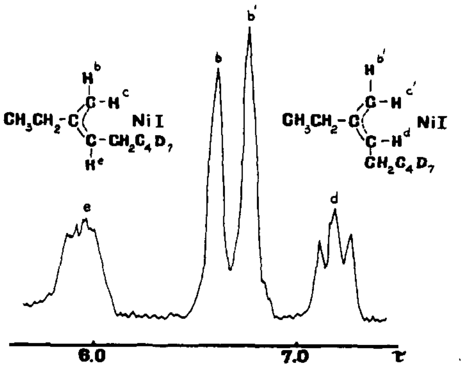


Figure 10. NMR spectrum (90-MHz) of a reaction mixture of $(C_4D_7NiI)_2$ and 2-ethylbutadiene (350 min, 20 °C). Initial concentrations: $[C_4D_7NiI] = 0.54$ M, $[C_6H_{10}] = 1.0$ M.

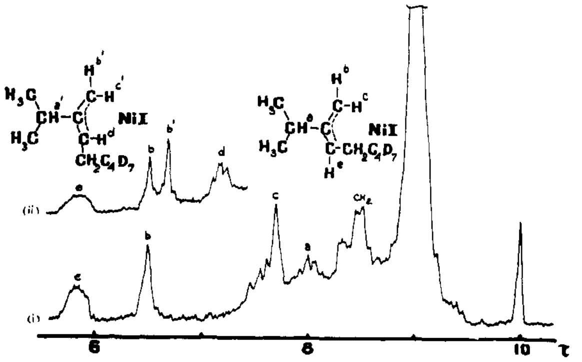
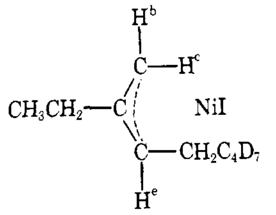
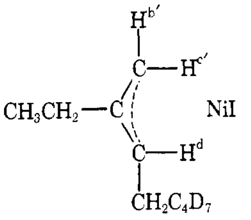


Figure 11. NMR spectra (90-MHz) of a reaction mixture of $(C_4D_7NiI)_2$ and 2-isopropylbutadiene. Initial concentrations: $[C_4D_7NiI] = 0.54$ M, $[C_7H_{12}] = 1.0$ M. Temperature, 20 °C. Time of interaction: (i) 1.5 h, (ii) 95 h.

a somewhat higher rate of the formation of 1:1 adduct having *anti*-1,2-disubstituted π-allylic ligand (IX) which gives rise to the following signals in the ^{1}H NMR spectrum: a singlet at τ 6.57 (H^b) and a widened resonance at τ 5.9 (H^e). Some time after there appear a singlet at τ 6.74 and a doublet of doublets at τ 7.18 due to H$^{b'}$ and H^d protons of syn complex X, respectively. The intensity of the two latter resonances gradually increases and eventually becomes higher than that of signals due to the anti complex. The ^{1}H NMR spectrum of the adduct of C_4D_7NiI and 2-ethylbutadiene recorded 350 min after the reagents were mixed is given in Figure 10. The intensity ratio of signals from H^b and H$^{b'}$ protons shows that by this moment about 55% of complex X and 45% of complex IX are present in the solution. In contrast to reactions with isoprene, adducts with 1,1-disubstituted π-allylic ligands were not observed in this case.



IX



X

The trend in the sequence of appearance of syn and anti isomers of 1,2-disubstituted π-allylic complexes in the solution observed when studying reactions with isoprene and 2-ethylbutadiene is even more pronounced in the reaction of C_4D_7NiI with 2-isopropylbutadiene. The ^{1}H NMR spectrum of the 1:1 adduct recorded 1.5 h after the reagents were mixed (Figure 11i) shows besides signals due to 1,3-diene the resonances of anti complex XI only: singlets from H^b (τ 6.47) and H^c (τ 7.67) protons, a widened resonance from a syn proton H^e (τ 5.8), a doublet from protons of *anti*-$CH_2C_4D_7$ group (τ 8.46), and a multiplet from H^a proton of the isopropyl group attached to the central allylic carbon atom (τ 8.0). Chemical shifts of the complex XI methyl protons were not assigned because of their shielding by a more intensive signal of the 1,3-diene methyl groups.

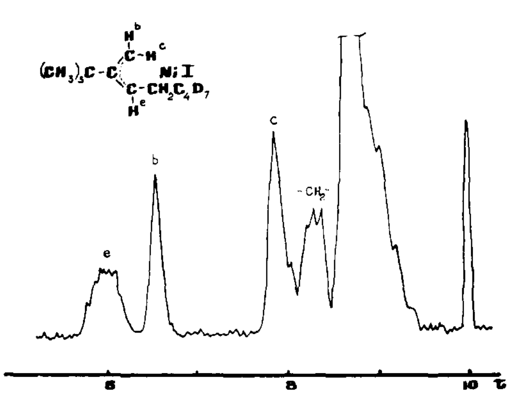
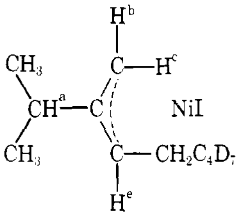
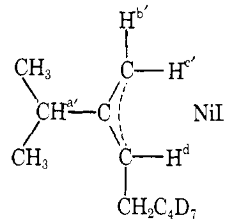


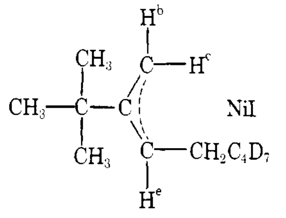
Figure 12. NMR spectrum (60-MHz) of a reaction mixture of $(C_4D_7NiI)_2$ and 2-*tert*-butylbutadiene (60 min, 25 °C). Initial concentrations: $[C_4D_7NiI] = 0.3$ M, $[C_8H_{14}] = 1.6$ M.



XI



XII



XIII

As the reaction proceeds, a marked amount of complex XII having syn structure appears in the solution, its proportion gradually increasing. Thus, the ^{1}H NMR spectrum of the reaction mixture $(C_4D_7NiI)_2$ + 2-isopropylbutadiene recorded 95 h after the reagents were mixed (Figure 11ii) shows that complex XII accounts for about 60% of the total amount of complexes formed in the solution. Typical signals which appear in the spectrum of complex XII are a singlet from H$^{b'}$ (τ 6.67) proton and a doublet of doublets from H^d (τ 7.16) proton.

When $(C_4D_7NiI)_2$ is reacted with 2-*tert*-butylbutadiene, a singlet at τ 6.45 (H^b) and a widened resonance at τ 5.8 (H^e) soon appear in the ^{1}H NMR spectrum (Figure 12), the resonances being typical of anti-1,2-disubstituted π-allylic complex XIII.

Reactions with 2,3-Dimethylbutadiene. The addition of C_4D_7NiI to symmetrical 1,3-diene–2,3-dimethylbutadiene can give only two isomeric 1,1,2-trisubstituted π-allylic complexes, XIV and XV.

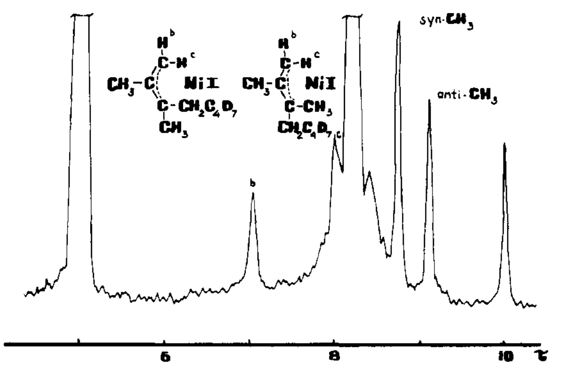


Figure 13. NMR spectrum (60-MHz) of a reaction mixture of $(C_4D_7NiI)_2$ and 2,3-dimethylbutadiene (130 min, 25 °C). Initial concentrations: $[C_4D_7NiI] = 0.40$ M, $[C_6H_{10}] = 2.3$ M.

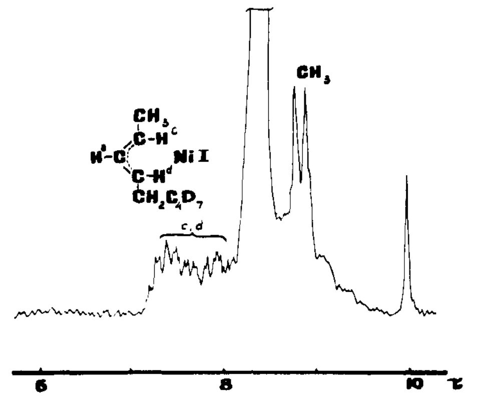
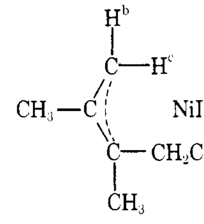
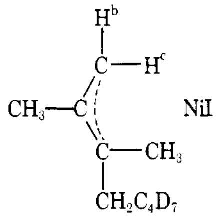


Figure 14. NMR spectrum (60-MHz) of a reaction mixture of $(C_4D_7NiI)_2$ and *trans*-1,3-pentadiene (9 h, 25 °C). Initial concentrations: $[C_4D_7NiI] = 0.40$ M, $[C_5H_8] = 2.3$ M.

The ^{1}H NMR spectrum of the reaction mixture (Figure 13) reveals both complexes present in the solution. This is evidenced by two singlet resonances in the high field, corresponding to *syn*- and *anti*-methyl groups at τ 8.75 and 9.10, respectively. An integral intensity ratio of about 2:1 indicates the anti complex XIV to be more preferable than syn isomer XV in this case. At the initial stages of the reaction such a ratio was still more favorable for the complex XIV. Resonances of *syn*-(H^b) and *anti*-(H^c) protons of complexes XIV and XV represent singlets at τ 7.0 and 8.0, respectively. Chemical shifts corresponding to methyl groups at the central allylic carbon atom were not calculated owing to the overlapping of this part of a spectrum by signals from methyl groups of 2,3-dimethylbutadiene.

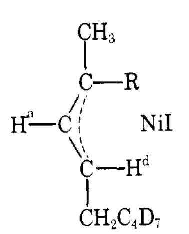


XIV

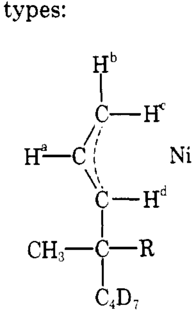


XV

Reaction with 1,3-Pentadienes and 4-Methyl-1,3-pentadiene. Theoretically, $(C_4D_7NiI)_2$ can react with these dienes to form complexes of two types:



XVI



XVII

R = H, CH_3

Complexes XVII should have a doublet of H^b proton at τ nearly 7.0 with coupling constant $J_{ab} = 7$ Hz. As these signals were not detected in the ^{1}H NMR spectra of 1,3-pentadiene and 4-methyl-1,3-pentadiene adducts with C_4D_7NiI one may conclude that in this particular case the 1,3-disubstituted (XVI, R = H) and 1,1,3-trisubstituted (XVI, R = CH_3) π-allylic complexes are the only products of this reaction.

The ^{1}H NMR spectrum of a 1:1 adduct of C_4D_7NiI and *trans*-1,3-pentadiene (Figure 14) shows two multiplets at τ from 7 to 8, corresponding to anti protons H^c and H^d of complex XVI, R = H. The 7 Hz doublet at τ 8.85 is indicative of the syn configuration of a methyl group. *cis*-1,3-Pentadiene gives the adduct of the same structure, but its reaction with $(C_4D_7NiI)_2$ proceeds with a lower rate.

4-Methyl-1,3-pentadiene interacts with $(C_4D_7NiI)_2$ to give complex XVI, R = CH_3. Unequivocal characteristics of this compound are: singlets of *syn*- and *anti*-methyl groups at τ 8.78 and 9.22, respectively; a doublet of a central allylic H^a proton at τ 5.28 ($J_{ad} = 12$ Hz) and a multiplet of H^d proton at τ 7.1 (Figure 15). Position of the last signal evidences the syn configuration of the π-allylic complex.

In systems containing 1,3-pentadienes, as in those with butadiene, we failed to detect the presence of anti structures in the adducts formed.

Discussion. Kinetic data on the reactions of the active site formation and the initial stages of polymer chain propagation[28] and also the distribution of the catalyst crotyl groups in macromolecules of various polymerization degree[29] lend further support to the conclusion concerning the polymerization of butadiene with $(C_4H_7NiI)_2$ as proceeding via a "living" chain mechanism with participation of dimeric forms of a starting complex and propagating macromolecules at least at the initial stages of *trans*-1,4-polybutadiene formation. Coordination of 1,3-diene molecules at these sites occurs via an associative mechanism involving the formation of intermediate five-coordinated complexes. In this case acceptor properties rather than the donor function of the monomer double bonds become more important. In alkyl-substituted 1,3-dienes, the unsubstituted double bonds display more pronounced acceptor abilities. Structures of C_4D_7NiI and these diene adducts suggest that the reaction of their formation may be formally considered as being a process of the complex insertion into a less substituted double bond of 1,3-diene.

Increased content of anti structures in the $(C_4D_7NiI)_2$ and 2-alkylbutadienes or 2,3-dimethylbutadiene adducts at the initial stages of reaction indicates high selectivity of the insertion process as to the anti structures formation. Syn isomers are formed as a result of anti–syn isomerization, its rate depending on the temperature and the nature of an alkyl substituent at a central allylic carbon atom. π-Allylic complexes containing a hydrogen atom at a central allylic carbon atom (products of $(C_4D_7NiI)_2$ reaction with butadiene, 1,3-pentadienes, and 4-methyl-1,3-pentadiene) are observed in ^{1}H NMR spectra only as syn complexes that may be due to the anti–syn isomerization running with a very high rate under our experimental conditions.

The rate of anti–syn isomerization was found to decrease

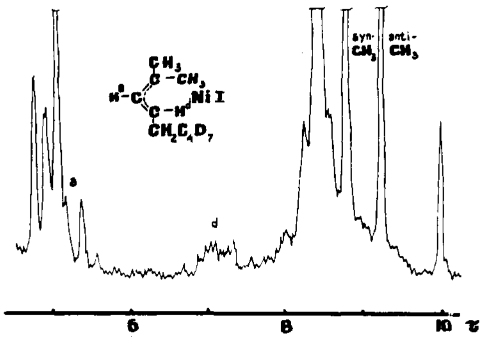


Figure 15. NMR spectrum (60-MHz) of a reaction mixture of $(C_4D_7NiI)_2$ and 4-methyl-1,3-pentadiene (33 h, 25 °C). Initial concentrations: $[C_4D_7NiI] = 0.40$ M, $[C_6H_{10}] = 2.3$ M.

depending on the nature of an alkyl substituent at a central carbon atom in π-allylic ligand in the following order:

$$H \gg CH_3 > C_2H_5 > i\text{-}C_3H_7 \gg tert\text{-}C_4H_9$$

that is, it decreases with increasing steric hindrances. The adduct of $(C_4D_7NiI)_2$ and 2-*tert*-butylbutadiene was found not to be isomerized to give a syn complex even under quite severe conditions. These regularities observed also in a series of 1,2-disubstituted π-allylic complexes of palladium[30-32] are accounted for by exclusively the steric interactions occurring between two substituents of the π-allylic ligand.

The appearance of anti complexes at the initial stages of the reaction is a general rule to which the reaction of 1,3-dienes insertion into metal–ligand bonds is subjected. Causality of the selectivity of these reactions is not yet clear.

Comparison of the ^{13}C NMR spectrum of bis(π-crotylnickel halides)[33] with the structure of 1,3-diene polymers prepared in their presence reveals the new carbon–carbon bond formation between most molecules of coordinated dienes and the most electronegative carbon atoms of a π-allylic ligand. In this case the polymer chain is built up of 1,4-units. Since in butadiene polymerization the end unit of a "living" macromolecule has only syn configuration, every monomer insertion results in the formation of namely trans-1,4 units.

In polymerization of isoprene, the end unit of a propagating polymer chain has mainly the structure of 1,2-disubstituted π-allylic complex of I or II type. The two end allylic carbon atoms of these complexes differ in their reactivities in the reaction with isoprene molecules as well as in polymerization of butadiene. Monomer insertion also takes place at the more electronegative unsubstituted carbon atom of π-allylic ligand in the complex I or II. In this case, if the structure of an end unit regenerates, the chain fragment composed of 1,4-units and separated from a metal attaches to the novel end unit, thus forming a head-to-tail structure. The content of cis- or trans-1,4 units in isoprene polymers should depend on the anti- and syn-π-allylic complexes of I or II type participation in the reactions of macromolecule chain propagation. Were these complexes of equal activity, the 1,4-cis and 1,4-trans units ratio in polymers might be dependent only upon the ratio of I and II complexes, respectively. But, according to ref 21, the content of cis-1,4 units in isoprene polymers synthesized in the presence of allylnickel halides is usually below the expected level, which may well be accounted for by various activities of anti- and syn-1,2-disubstituted π-allylic complexes.

The data of Table I show that the signals of H^b and H^c protons of the anti complex I appear in the field by 0.2 and 0.6 ppm lower than those of $H^{b'}$ and $H^{c'}$ protons of the syn complex II. Net value of about 0.8 ppm is indicative of the appreciable decrease in electron density at the unsubstituted allylic carbon atom as compared with syn complex. Since the syn–anti isomerism has less bearing upon the shielding of substituted end allylic carbon atom, one may conclude that the difference in electron densities of the two end allylic carbons at the active sites of an anti structure is less pronounced than that of a syn isomer. Such an electron density distribution in the anti complexes may lead to some increase in the relative proportion of the reaction of isoprene insertion into a nickel-substituted allylic carbon bond thus resulting in the formation of 3,4-units in polymeric chains. Increasing size of alkyl substituent at a central allylic carbon leads to an increase in anti complex concentration in the solution. Both these factors are evidently responsible for the growth of 3,4-units content in a series of polymers of isoprene, 2-ethylbutadiene, and 2-isopropylbutadiene synthesized by the use of $(C_4H_7NiI)_2$, from 6 to 14 and 22%, respectively.[21]

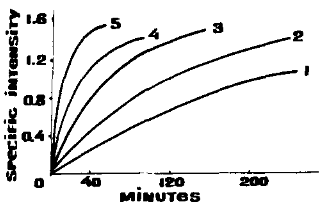


Figure 16. Kinetic curves of the formation of 1:1 adducts of C_4D_7NiI and 1,3-dienes. Initial concentrations: $[C_4D_7NiI] = 0.35$ M, [diene] = 2.15 M. Temperature, 23 °C. Dienes: (1) butadiene; (2) isoprene; (3) 2-ethylbutadiene; (4) 2-isopropylbutadiene; (5) 2-*tert*-butylbutadiene.

The nature of 2-alkyl substituent has a great influence upon both the direction of its reaction with π-crotylnickel iodide and the rate of the 1:1 adduct formation. Kinetic curves derived for the reactions of stoichiometric addition of C_4D_7NiI to various dienes (Figure 16) show that these diene activities increase in the order:

$$C_4H_6 < C_5H_8 < C_6H_{10} < C_7H_{12} < C_8H_{14}$$

The rates of the second and other diene molecules insertion to the respective 1:1 adduct vary in the opposite direction, as is evidenced by the relative activities of the first four monomers in the course of polymerization. The observed regularities agree well with the order of variation in the metal–π-allylic ligand bond strength as a function of the nature of a substituent at a central allylic carbon atom.

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Polymerization of Butadiene by η^3-Crotylbis(triethylphosphite)nickel(II) Hexafluorophosphite

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ABSTRACT: By a combination of kinetic and molecular weight studies the title reaction was shown to be complicated by decomposition of the initially active catalyst, **1**, into more active transient species, **2**, and finally into a stable species, **3**, with an activity comparable to that of **1**. Molecular weight distributions, measured by gel permeation chromatography, showed that **1** and **3** and part of **2** produce low molecular weight *trans*-1,4-polybutadiene ($\overline{M}_n \sim 5000$) similar to that produced by allylnickel iodides. Part of the more reactive transient species, **4**, produces a polymer fraction of much higher molecular weight ($\overline{M}_n \sim 100\,000$). Such high molecular weight fractions were absent from polymer produced by catalyst solutions that had been preheated to 90 °C for several hours. The heating of **1** in the absence of butadiene appears to convert it to **3**. At 90 °C the complex **1** reacts with added triethylphosphite to produce diethyl ether. The transitory nature of the inhibiting effect of added triethylphosphite on the polymerization rate is attributed to the removal of the phosphite by the latter reaction.

The stereospecific polymerization of 1,3-dienes by transition organometallic catalysts has been the subject of intensive investigation for over 20 years, and at the synthetic level this work has been very fruitful. In fact almost any desired stereo or positional microstructure for simple 1,3-dienes can be achieved by choice of the appropriate catalyst.[1,2] The evolution of understanding, at a detailed mechanistic level, of the processes governing stereoselectivity and degree of polymerization has been much slower.

One of the major barriers to success in this problem is the difficulty in finding systems which are valid models for active polymerization catalysts yet have the necessary chemical and physical properties to allow direct observation of the insertion process. This difficulty is exemplified by the fact that insertion reactions of allylpalladium complexes can be investigated in great mechanistic detail[3] but they are relatively poor models for polymerization catalysts since they show neither great versatility, nor activity for diene polymerization. On the other hand, allylnickel complexes show considerable versatility and activity in polymerization, but their greater reactivity and lower stability make application of the methodology used in allylpalladium chemistry to probe the details of the insertion mechanism difficult or impossible to apply.

The allylnickel halide system held early promise that the riddle of stereoselectivity would be easily solved.[4-6] The allylnickel halides are relatively stable and polymerize butadiene by a fairly uncomplicated mechanism. Most striking however is the great effect the minor structural change of replacing chloride with iodide has on the stereoselectivity.[5] The early promise of this model has not been realized, in spite of some ingenious experimentation,[7,8] mainly because it is impossible to observe the primary insertion product of the reaction. The active species in these systems are monometallic but the bulk of the nickel sites are in the form of resting dimer and it is these species which are observed by physical methods such as NMR.[7,8] Similar hopes and problems were characteristic of studies on the allylnickel acetate and haloacetate catalysts.[9]

In the present paper we present results of a study of the polymerization of butadiene by η^3-crotylbis(triethylphosphite)nickel(II) hexafluorophosphate, **1**. This compound has been extensively studied as a catalyst for the codimerization of ethylene/butadiene.[10] In a footnote it was reported that this catalyst produced a white waxy solid, presumed to be polybutadiene, when heated with butadiene.[10] This observation was confirmed in our laboratory and the product was shown to be *trans*-1,4-polybutadiene (>95%). The complex, **1**, seemed very attractive as a possible model for studying the stereochemistry of diene insertion under polymerization conditions. It is monomeric, easy to synthesize and purify, and gives the appearance of being quite stable in the absence of oxygen.

Results

Selection of Solvent. The choice of a solvent for the polymerization of butadiene by **1** was restricted by three factors.