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CATALYTIC REGULAR POLYMERIZATION OF PROPADIENE AND ALKYLPROPADIENES

SEI OTSUKA,* K. MORI, T. SUMINOE and F. IMAIZUMI

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka City, Osaka, Japan
and
Research Laboratory, Japan Synthetic Rubber Co. Ltd., Yokkaichi City, Mie, Japan

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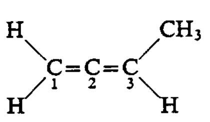
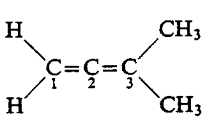
Abstract—Catalytic linear polymerizations of propadiene, 1,2-butadiene, and 3-methyl-1,2-butadiene were achieved with low-valent-nickel complexes as homogeneous catalysts. Interaction of propadiene with some iron, cobalt, and nickel complexes produced propadiene complexes of various stabilities. Isolated complexes involving metal-stabilized-radical-ligands were noted as the possible initiating species. Labile propadiene complexes of Ni(O) and Co(O) atoms are generally active for the catalytic polymerizations. Several factors determining the catalytic activities were discussed. The i.r. and NMR spectra revealed that the polymers obtained with the nickel catalysts are of quite regular structures. The polymer structures of asymmetrically substituted propadienes suggested that a regular propagation takes place preferentially at the unsubstituted double bond which participates in the co-ordination to metal.

INTRODUCTION

PROPADIENES can be polymerized by various means. However, probably because of the cumulated double bonds subject to simultaneous excitation by radical or ionic reagents, the polymerizations are generally accompanied by cross-linking. For example, the polymerization of propadiene with Ziegler type catalysts containing $VOCl_3$ and other transition metals yields polymers insoluble in benzene.(1) The propadiene polymer without cross-linking has been prepared recently with π-complexes of low valent nickel.(2) This permitted us to perform detailed studies of the polymer microstructures. The synthesis has now been extended to 1,2-butadiene and 3-methyl-1,2-butadiene. For these asymmetrically substituted propadienes there are two possible modes of addition, viz. 1,2- and 2,3-polymerization.



$H_2\underset{1}{C}=\underset{2}{C}=\underset{3}{C}H(CH_3)$



$H_2\underset{1}{C}=\underset{2}{C}=\underset{3}{C}(CH_3)_2$

A question then arises as to which double bond remains intact or participates in a propagation of catalytic polymerizations. Of particular interest is the question of whether the double bond co-ordinated to the catalyst metal takes part in the propagation or whether the reaction involves the neighbouring double bond. The structural data for these polymers are expected to shed some light on the above problem.

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* Enquiries to this author at the Osaka University.

Another purpose of this paper is to present some observations on the transition metal-initiated polymerization of the three allenes. On the basis of the observations, there will be discussion of some factors affecting the overall polymerization rates and the catalytic activities.

EXPERIMENTAL

Materials

Commercial propadiene of 98·75 per cent purity was dried over molecular sieve 4A and distilled before use. The impurity includes methyl-acetylene (0·55%), propene (0·33%) and 1,3-butadiene (0·37%). 1,2-Butadiene of 95·4 per cent purity was prepared from 1,2,3-tribromobutane.(3, 4) 3-Methyl-1,2-butadiene was derived from 3-methyl-3-hydroxy-1-butyne.(5) The methyl-butynol was converted into 3-methyl-3-chloro-1-butyne(6) in 92 per cent yield which was then treated with zinc-copper couple(7, 8) to give the methylbutadiene in 60 per cent yield. Preparative gas chromatography improved the purity to 99·4 per cent.

Catalyst complexes prepared according to known methods were bis(1,5-cyclooctadiene)nickel(O)(9), bis(π-allyl)nickel(O),(10) bis(acrylonitrile)nickel(O),(11) iodo(π-allyl)nickel(I),(12) and chloro(triphenylphosphine)-π-allylnickel(I).(13, 14) The following were derived from bis(1,5-cyclooctadiene)nickel-(O):(14) Tetrakis(*tert*.-butyl-isonitrile)nickel(O), chloro(π-allyl)nickel(I)(15) and 2,2′-bipyridyl(1,5-cyclooctadiene)nickel(O). Commercial bis(acetylacetonate)nickel(II) recrystallized from benzene-n-hexane and dibromobis(triphenylphosphine)nickel(II) prepared by L. M. Venanzi's method(18) were dried at 100° under vacuum. Tris(π-allyl) cobalt was prepared according to G. Wilke.(16, 17) Commercial triethylaluminum was used without further purification. For solvents, pure grade deaerated benzene and toluene were used.

Physical measurements

Infra-red spectra were measured by a Model DS-402G grating spectrophotometer of Japan Spectroscopic Co. Ltd. and NMR spectra by a high resolution 100 Mc Model JNM 4H-100 of the Japan Electron Optics Lab. Number average molecular weights were measured by a membrane osmometer of Mechrolab Model 502 using toluene as a solvent.

Polymerization procedure

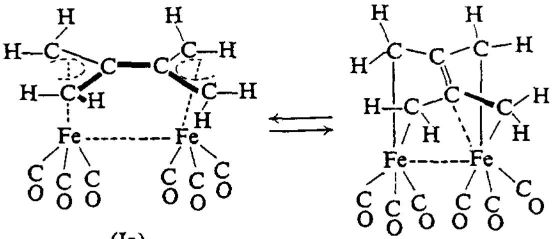
All manipulations involving organometallics were carried out under pure nitrogen. In a glass ampoule connected to a high vacuum system were placed a nickel complex and benzene, followed by the introduction of the required amount of monomer at $-78°$ (see Table 1). The ampoule was sealed and placed in a thermostat bath for polymerization. Polymers were isolated as usual using 2,2′-methylene-bis(4-methyl-6-*tert*.-butylphenol) as an anti-oxidant and were reprecipitated from benzene in methanol before spectroscopic measurements.

RESULTS AND DISCUSSIONS

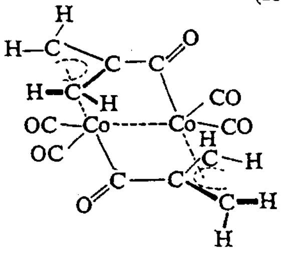
Catalytic polymerizations

a. Complex formation relating to the initiation. As has been reported before, labile π-complexes of low valent nickel and cobalt are effective for polymerization of propadiene under relatively mild conditions in an inert atmosphere. This was found to be the case also for 1,2-butadiene and for 3-methyl-1,2-butadiene. They represent typical examples of co-ordination polymerization which can be effected with homogeneous catalysts yielding polymers of highly regular microstructures. Closely related is the complex formation reaction by ligation of a monomer. Thus the interaction of propadiene with some iron or cobalt carbonyls under appropriate reaction conditions affords relatively stable propadiene complexes. Iron pentacarbonyl, which is too inert to be an initiator for the polymerization, showed no reaction with propadiene below 40°. From the reaction of triiron dodecacarbonyl and propadiene at 80°, however, Nakamura and Hagihara(18) were able to isolate a stable propadiene iron carbonyl complex, $C_6H_8Fe_2(CO)_6$ (Ia,b). Valence tautomerism involving the two forms, Ia and Ib, was postulated to explain the NMR spectrum of the C_6 ligand.(18)

The polymerization activity of dicobalt octacarbonyl for propadiene had already been recognized.(19) The polymerization can be effected at 40° producing insoluble polymers of unknown structures. The reaction of a limited amount of propadiene with the carbonyl at 30–40° affords the propadiene cobalt carbonyl complex (II) which shows polymerization activity towards propadiene.(18)



(Ia) (Ib)



(II)

These isolated complexes (Ia, Ib, and II), whose structures are shown involving metal-stabilized-radical-ligands, seem to correspond to one of the possible initiating species.

The interaction of propadiene with some nickel(O) complexes produced labile complexes. For example, bis(1,5-cyclooctadiene)-nickel(O), [Ni(COD)$_2$], was dissolved in liquid propadiene below −30° to give a clear-red solution from which was precipitated a dark-red crystalline complex below −70° when excess propadiene was distilled off. Gas chromatography of the liquid phase indicates the presence of 1,5-cyclooctadiene. The complex was found to be extremely air sensitive and very active for the initiation of propadiene-polymerization above 5°.(2) However, because of the instability of the complex, its structure has not yet been elucidated. Isolation of a propadiene-nickel(I) halide complex was impossible from a reaction of propadiene with bromo(π-allyl)nickel.

b. Factors determining the catalytic activities. Besides Ni(COD)$_2$, the following nickel complexes were all effective for the polymerization: Bis(π-allyl)nickel(O), tetrakis(*tert*.-butylisonitrile)nickel(O), bis(acrylonitrile)nickel(O), halogeno(π-allyl)-nickel(I), and chloro(π-allyl)(triphenylphosphine)nickel(I). A common feature for these complexes is the ready substitution of the organic ligands by propadiene. Complete replacement of organic ligands can be seen in the case of Ni(COD)$_2$, while the halogen ligands in halogeno(π-allyl)nickel(I) appears to remain on the Ni(I) ion during the polymerization. As shown in Table 1, the Ni(I) catalyst is much more active than the Ni(O) complex. The failure to isolate a propadiene nickel(I) halide complex and

TABLE 1. POLYMERIZATION OF PROPADIENES WITH BIS(1,5-CYCLOOCTADIENE)NICKEL(O) AND WITH BROMO(π-ALLYL)NICKEL(I)

Catalyst		Reaction conditions*		Polymer yield (%) of		
Complexes	(mmole)	(°C)	(hr)	$CH_2=C=CH_2$	$CH_3CH=C=CH_2$	$(CH_3)_2C=C=CH_2$
$Ni(C_8H_{12})_2$	0·04	40	2	trace	3·7	12·5
	0·08	40	6	6·2	9·3	22·0
$(C_3H_5NiBr)_2$	0·02	0	0·5	6·3	27·2	7·8
	0·02	0	1	13·3	43·8	15·0
	0·02	20	1	65·1	94·5	71·3

* The total volume of the reaction mixture containing 20 mmoles of a monomer was 11 ml and the solvent was benzene for all polymerizations.

the enhanced polymerization activity suggest that the halogen anion attached to the Ni(I) ion labilizes the π-co-ordination of propadiene; an analogous role of halogens for the metal-carbonyl bondings in carbonyl halide complexes of 3*d* transition metals has already been recognized and theoretically interpreted.(20, 21) Table 2 indicates the effect of nature of halogens in the nickel(I) catalysts for polymerization of 1,2-butadiene. The relative rate, expressed qualitatively by the polymer yields, increases in the order of $Cl < Br < I$. This is the order of increase in the π-polarizability of halogens(20) which should affect an energy level difference between the highest-filled and the lowest-vacant π-orbitals involved in an intermediate complex. However, paucity of experimental evidence at present does not allow us to assign any unambiguous meaning to the role of the π-polarizability in the catalysis.

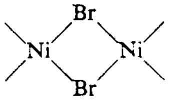
TABLE 2. POLYMERIZATION OF 1,2-BUTADIENE WITH HALOGENO(π-ALLYL)NICKEL(I) AND WITH CHLORO(π-ALLYL)(TRIPHENYLPHOSPHINE)NICKEL(I)

Catalyst		Reaction conditions*		Polymer yield	Polymer structure	
Complexes	(mmole)	(°C)	(hr)	(%)	2,3-/1,2-	$\bar{M}_n$
$(\pi\text{-}C_3H_5NiCl)_2$	0·1	0	1	12·3	10/90	—
$(\pi\text{-}C_3H_5NiBr)_2$	0·1	0	1	62·3	13/87	$6{\cdot}6\times10^4$
$(\pi\text{-}C_3H_5NiI)_2$	0·1	0	1	99·5	21/79	—
$(\pi\text{-}C_3H_5)(PPh_3)NiCl$	0·1	40	4	9·5	11/89	—

* The total volume of the reaction mixture containing 100 mmole of a monomer was 55 ml and the solvent was benzene for all polymerizations.

In contrast to the halogens, such ligands as triphenylphosphine and 2,2′-bipyridyl appears to exert a stabilizing effect for the co-ordination of propadiene. Ligation of triphenylphosphine to the Ni(I) halide ion reduces the activity as implied in Table 2. Interaction of propadiene with blue violet 2,2′-bipyridyl(1,5-cyclooctadiene)nickel-(O)(14) in n-pentane at −20° to −30° produced a dark-greenish bipyridyl nickel(O) complex containing propadiene ligand, but no polymerization was observed in the presence of a catalytic amount of the bipyridyl(COD)nickel complex. The stabilization effect of the bipyridyl ligand for propadiene-co-ordination is evident. In addition to this effect, the chelate ligation should reduce the availability of co-ordination sites of the Ni(O) atom.

Availability of co-ordination sites in a catalyst metal is an important steric factor often governing the catalytic activity. Two factors must be taken into account for the availability; one is the steric requirement of an original ligand which retains its co-ordination during the catalysis, and the other is that of a growing chain-end and of an in-coming monomer. The observed relative rates for the three propadienes in the $Ni(COD)_2$-catalysed polymerization increases in the order of propadiene < 1,2-butadiene < 3-methyl-1,2-butadiene (Table 1). Because the two cyclooctadiene ligands of $Ni(COD)_2$ are readily replaceable by the monomers leaving nickel(O) species free from the sterical effect of the original ligand, the result may be interpreted in terms of $d\pi$-accepting abilities of the monomers, i.e. the order represents an increase in lability of co-ordination of the monomers. For the polymerizations catalysed by bromo(π-allyl)nickel, however, the rate was in the order propadiene < 3-methyl-1,2-butadiene < 1,2-butadiene (Table 1). A possible explanation for the reversed order for the substituted propadienes, is that in the binuclear halogen-bridged nickel(I) complex only limited co-ordination sites, probably two, are available for each Ni(I) ion because of occupation by the halogens, i.e. in this case the steric requirement is assumed to be of greater influence than the $d\pi$-accepting properties of the monomer.



The extremely labile complex, $Co(C_3H_5)_3$, was found active at a temperature as low as − 10° yielding polypropadiene of which the i.r. spectrum was essentially identical with that of the polymer obtained with nickel(O) complexes, although the cobalt-catalysed polymer was again insoluble in organic solvents.

While the complexes containing low-valent nickel and cobalt are active catalysts, those containing the metal ions in higher oxidation states lack activity. For example, a benzene solution of propadiene was heated at 40° in the presence of dibromobis-(triphenylphosphine)nickel(II) but neither the polymer nor an isolable propadiene complex was found. When a benzene solution of propadiene containing bis(acetyl-acetonate)nickel(II) as a catalyst was heated at 40°, the pale green colour of the homogeneous solution changed to light yellow indicating ligation of the monomer, but again no polymerization was detected. Thus in these co-ordination polymerizations the $d\pi$-donation from a metal into a vacant $p\pi$-orbital, i.e. a low-lying anti-bonding orbital, of a monomer should be responsible for the "opening" of the double bond which leads to polymerization.

c. The double bond taking part in the propagation. From the point of view of the $d\pi$-accepting ability as well as of the steric factor, the participation of the methyl-substituted 2,3-double bond in the co-ordination appears to be unlikely. The polymer structure of these substituted propadienes is therefore of considerable interest with respect to the question of which double bond participates in the propagation. The polymers were always of 1,2-structures, as described in the subsequent section, indicating that the double bond which took part in the propagation is the one co-ordinated to the catalyst metal.

Chemical structures

This section describes mainly the chemical structures of the three polypropadienes based on spectral data.

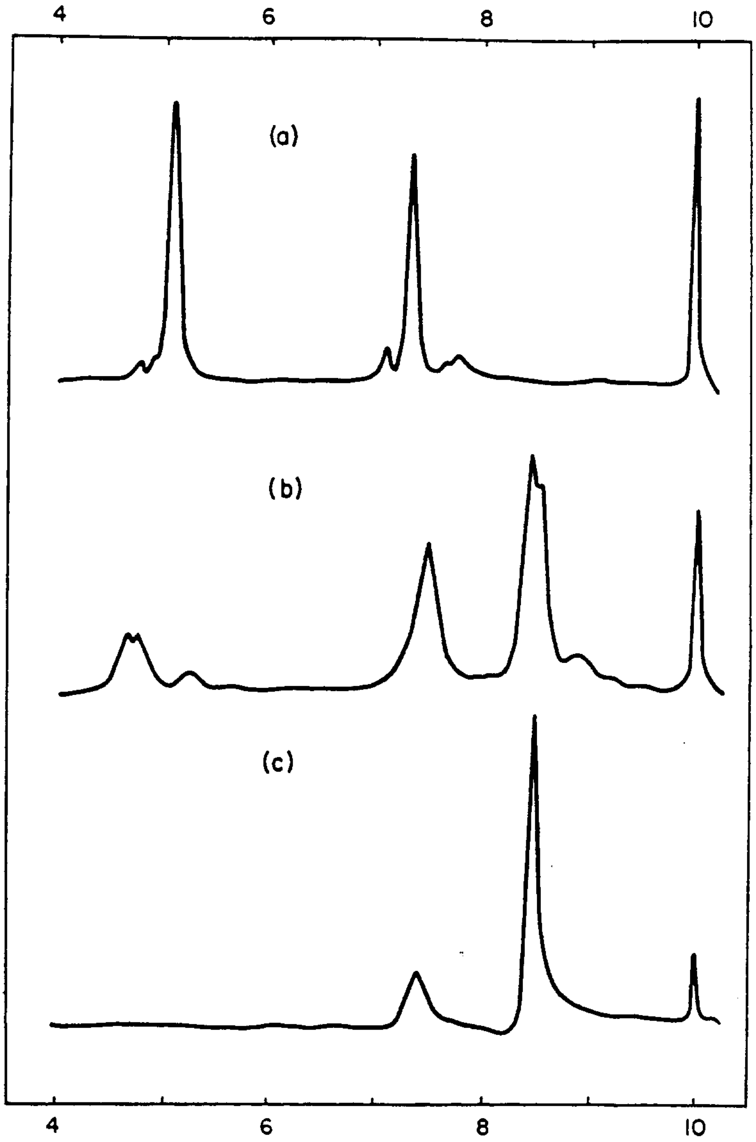


FIG. 1. NMR spectra of polypropadienes obtained with nickel catalysts. (a) polypropadiene; (b) poly-1,2-butadiene; (c) poly-3-methyl-1,2-butadiene.

a. Polypropadiene. The proton NMR spectrum (Fig. 1a) shows two intense absorptions (singlet) at τ 7·31 ($—CH_2$) and 5·05 ($=CH_2$) of an approximately equal integral value. In the i.r. spectrum (Fig. 2a) the out of plane deformation of $=CH_2$ (vinylidene), the $—CH_2$-bending deformation, $C=C$ stretching, and C—H stretching are observed at 897, 1426, 1636 and 2900–3100 cm^{-1}, respectively. These spectral data led us to con-

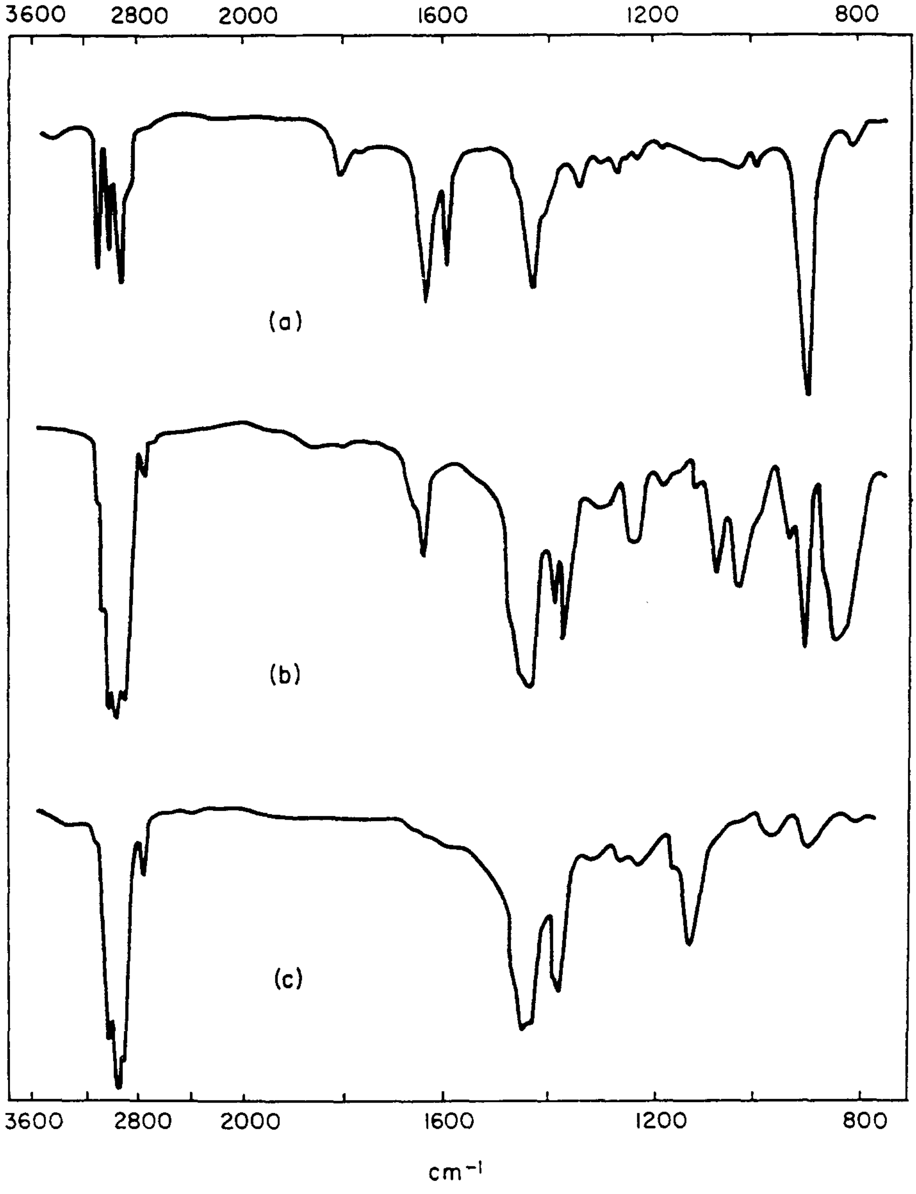
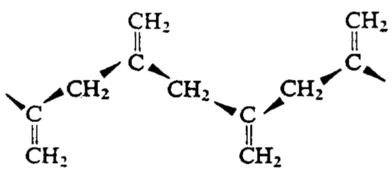


FIG. 2. Infra-red spectra of polypropadienes obtained with nickel catalysts. (a) polypropadiene; (b) poly-1,2-butadiene; (c) poly-3-methyl-1,2-butadiene.

clude that the predominant structural unit must be vinylidene and methylene groups, and that therefore the repeating sequence is —[CH_2—C(=CH_2)—]$_n$. This was substantiated by X-ray analysis[22] which showed good agreement between the observed



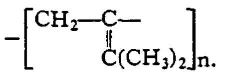
diffraction data and the calculated diffraction intensities based on an assumption of 2/1 helix for the polymer chain.

The number average molecular weight of the 1,2-polypropadiene obtained with the Ni(I) catalysts ranged from $1{\cdot}0 \times 10^5$ to $1{\cdot}4 \times 10^5$ depending on the reaction conditions. It is the halogeno(π-allyl) nickel(I) complexes that most readily produce polymers of higher molecular weight. In general the molecular weight tends to increase with increase in the initial monomer concentration, with decrease in the catalyst concentration, and with lowering the polymerization temperature as has frequently been experienced in catalytic polymerizations.

Ziegler type catalysts covering nearly all 3*d* transition metals including nickel generally gave insoluble propadiene polymers. The polypropadiene obtained with some Ziegler catalysts has nevertheless been shown to be of quite regular structure; for example, the one obtained with the $AlEt_3$–$VOCl_3$ system exhibited a highly crystalline X-ray diffraction pattern definitely clearer than that of the nickel-polymer.(23) The nickel-polypropadiene, which is doubtlessly quite linear, appears to contain some structural impurities. The unidentified C=C stretching absorption at 1596 cm^{-1} and also some minor NMR absorptions in the region of the two main resonances may be due to these impurities. The impurities responsible for defects in the crystalline structure are considered to be responsible for the low melting point (62–63°) and the solubilities in a wide variety of organic solvents.(2)

It may be of interest to note that the polymer microstructure as a rule is not influenced by the formal oxidation states of the catalysts, i.e. Ni(O) and Ni(I), and by their original organic ligands, provided they are readily replaceable by the monomer; however the degree of regularity estimated from the i.r. spectra was subject to slight changes depending upon these factors (Table 2).

b. Poly-3-*methyl*-1,2-*butadiene.* The NMR spectrum (Fig. 1c) is the simplest one showing two peaks (singlet) at τ 8·46 and 7·40 with an intensity ratio of 3/1. These are readily assigned to the protons of $(CH_3)_2C=$ and $—CH_2—$ respectively. In the C=C stretching region two weak i.r. absorptions appear at 1635 and 1595 cm^{-1}, the latter being stronger than the former. These bands tend to diminish, for unknown reasons, upon treatment such as dissolution and precipitation or film formation. Further studies are necessary for the assignments. Other absorptions tentatively assigned are the $—CH_2—$bending deformation at 1440 cm^{-1}, asymmetric and symmetric $CH_3—$ bending at 1425 and 1365-75 cm^{-1}, CH_3 rocking modes at 1122 cm^{-1}, and out of plane deformation of $=CH_2$ at 890 cm^{-1}. The last absorption, which should be an intrinsically intense band, was very weak indicating the vinylidene structure to be present in only a trace amount. This is in agreement with the NMR spectrum described above. Consequently, the polymer appears to be composed almost entirely from the unit,

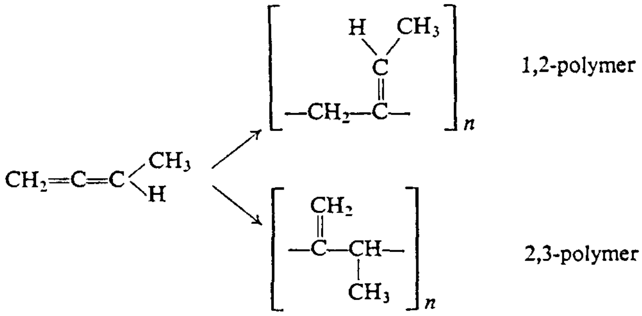


$$-\left[CH_2-\underset{\substack{\| \\ C(CH_3)_2}}{C}-\right]_n.$$

It can be regarded as the most regular polymer among the three and the regularity was retained for both cases of the Ni(O) and Ni(I) catalysts. Studies on the crystal structure are now being performed by Tadokoro's group in Osaka University.(23)

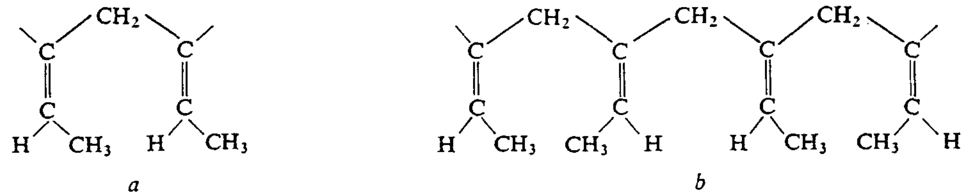
The number average molecular weight of the polymer obtained under a comparable polymerization condition (see Table 1) was the smallest ($2 \sim 4\times10^4$) among the three polypropadienes.

c. Poly-1,2-*butadiene.* The NMR spectrum of the polymer obtained with the $Ni(COD)_2$ catalyst under the conditions given in Table 1 is a little complicated as shown in Fig. 1b. The peaks at τ 8·45 (doublet), 7·44 (singlet), and 4·64 (quartet) are readily assigned to the methyl proton of $=CH—CH_3$, the methylene proton of $—CH_2—C(=CHCH_3)—$, and the inner olefinic proton of $=CH—CH_3$, respectively. The weak signal at τ 5·16 is probably due to protons of $=CH_2$ group, since the polypropadiene shows a resonance at τ 5·05 for the same protons. If the signal at τ 5·16 is ascribed to the vinylidene protons, a ratio of the two resonance integrals, $I_{5\cdot16}/I_{7\cdot44}$ should indicate the ratio of 2,3-/1,2-structure, and this should also be the case for the two types of methyl protons which



belong to the respective structures. The relatively weak signal at the higher field ($\tau = 8{\cdot}85$) is a doublet probably due to the methyl proton of $—CH(CH_3)—$ group in the 2,3-polymer. Then, the integral ratio $I_{5\cdot16}/I_{7\cdot44}$ should be reflected in the ratio of the two types of methyl protons, $I_{8\cdot85/8\cdot45}$. In fact, the two estimated ratios were found to be approximately equal (13/87) supporting the above assignments. Thus the 1,2-unit may be calculated to be 87 per cent of the total structural unit. In accord with the NMR spectrum, Fig. 2b shows that the out of plane deformation of vinylidene (895 cm^{-1}) appears in medium intensity. In addition to this, out of plane deformation of $=CH$, probably of $C=C\begin{smallmatrix}H\\CH_3\end{smallmatrix}$, appears at 835 cm^{-1}. The $—CH_2—$ bending or scissoring and the CH_3-bending absorptions are more or less similar to that of poly-3-methyl-1,2-butadiene. In the $C=C$ stretching region there occur also two bands at 1637 and 1660 cm^{-1}, the latter being a shoulder of the former. Again these bands have yet to be assigned.

It may be pertinent to point out here an interesting stereoisomerism for the poly-1,2-butadiene shown below.



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The configurations *a* and *b* are somewhat analogous to the *iso-* and syndiotactic structures. In addition to these, there should also be a random configuration corresponding to an atactic structure. So far, we have been unable to isolate any of these polymers.

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Résumé—On a préparé des polymères linéaires par polymérisation du propadiène, du butadiène-1,2 et du méthyl-3 butadiène-1,2 en utilisant comme catalyseurs homogènes des complexes du nickel à faible valence. L'interaction du propadiène avec des complexes du fer, du cobalt et du nickel donnait des complexes du propadiène avec des stabilités variées. Des complexes isolés comprenant des ligands radicalaires stabilisés par des métaux ont été considérés comme agents d'amorçage possibles. Les complexes atomiques instables du propadiène avec Ni(O) et Co(O) sont généralement actifs pour des polymérisations catalytiques. Plusieurs facteurs qui déterminent l'activité catalytique sont discutés. Les spectres i.r. et RMN ont montré que les polymères obtenus avec des catalyseurs au nickel avaient des structures assez régulières. Les structures des polymères de propadiènes substitués assymétriques suggèrent que la propagation régulière se produit préférentiellement sur la double liaison non substituée qui participe à la coordination de métal.

Sommario—Si sono ottenute polimerizzazioni catalitiche lineari del propadiene, dell'1,2-butadiene e del 3-metil-1,2, butadiene usando come catalizzatori omogenei complessi del nichel a bassa valenza. L'interazione del propadiene con alcuni complessi del ferro, del cobalto e del nichelio dà luogo a complessi del propadiene a varie stabilità.

Come specie iniziatrice vengono osservati complessi isolati con legandi radicalici stabilizzati dal metallo. Nelle polimerizzazioni catalitiche sono attivi in generale complessi labili degli atomi di Ni(O) e Co(O) col propadiene. Vengono discussi i diversi fattori che influenzano l'attività catalitica. Dagli spettri i.r. e NMR si vede che i polimeri ottenuti con catalizzatori al nichelio hanno struttura completamente regolare. La struttura dei polimeri dei propadieni sostituiti asimmetricamente fa pensare che una propagazione regolare avvenga preferenzialmente sul doppio legame privo di sostituenti che partecipa nella coordinazione del metallo.

Zusammenfassung—Katalytische lineare Polymerisation von Propadien, 1,2-Butadien und 3-Methyl-1,2-butadien wurde mit niederwertigen Nickelkomplexen als homogenen Katalysatoren erreicht. Die Wechselwirkung von Propadien mit einigen Eisen-, Kobalt- und Nickelkomplexen führte zu Propadienkomplexen verschiedener Stabilität. Isolierte Komplexe, an denen Metall-stabilisierte Radikalliganden beteiligt waren, wurden als mögliche initiierende Einheit festgestellt. Labile Propadienkomplexe von Ni(O) und Co(O) Atomen sind allgemein für die katalytischen Polymerisationen aktiv. Es wurden einige die katalytischen Aktivitäten bestimmende Faktoren diskutiert. I.R.- und NMR-Spektren zeigten, daß die mit Nickelkatalysatoren erhaltenen Polymeren sehr regelmäßige Strukturen haben. Die Polymerstrukturen von asymmetrisch substituierten Propadienen ließen vermuten, daß ein regelmäßiges Wachstum bevorzugt an der unsubstituierten Doppelbindung, die in Koordination zum Metall steht, erfolgt.