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Stereospecific Polymerization of Butadiene by Catalysts Prepared from π-Allyl Nickel Halides

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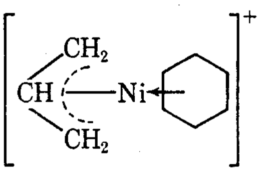
Synopsis

Butadiene has been polymerized by π-allyl-Ni-halides (I) to low molecular weight stereoregular polymers, with either benzene, *n*-pentane, tetrahydrofuran, cyclohexanol, or ethyl alcohol used as solvents. Solid polymers and oily products were simultaneously obtained as polymerization products. In benzene as solvent, π-allyl-Ni-I and π-allyl-Ni-Br gave predominantly *trans*-1,4 polymers, while π-allyl-Ni-Cl gave polymers largely composed of *cis*-1,4 units. In the other solvents predominantly *trans*-1,4 polymers were obtained, irrespective of the nickel derivative used. By reacting π-allyl-Ni-Br, in benzene solution, with either $AlBr_3$, $Al_2(O\text{-}i\text{-}C_3H_7)_3Br_3$, BF_3 or $TiCl_2\ (O\text{-}i\text{-}C_3H_7)_2$, complexes were obtained (II) which polymerize butadiene to predominantly *cis*-1,4 polymers. Evidence is reported that these complexes are of ionic type and contain the cation



The different stereospecificity observed in the polymerizations by I and II is interpreted on the basis of the different mode of coordination of butadiene to Ni of the complexes I and II, respectively.

Many facts support the hypothesis that the catalysts obtained from aluminum alkyls and transition metal compounds are bimetallic complexes containing both the aluminum and the transition metal. It is believed that in the polymerization of conjugated diolefins by these catalysts, the polymer chain grows by insertion of the monomer on the π-allylic bond between the transition metal and the last polymerized unit.

In view of this, it appeared of interest to examine the polymerization of conjugated diolefins by simple π-allyl derivatives of transition metals, in the absence of aluminum alkyls. It was expected that the use, as catalysts, of these compounds would provide useful information concerning the nature and mechanism of the more complex catalysts obtained from aluminum alkyls and transition metal compounds.

Some examples of polymerization or oligomerization of butadiene by π-allyl derivatives of transition metals have already been reported in the literature. Wilke trimerized butadiene to cyclododecatriene by bis-π-allyl-Ni.[1] In a preliminary communication, we reported the polymerization of butadiene to crystalline *trans*-1,4-polymers by π-allyl-Ni-Br.[2] Wilke polymerized butadiene by chromium and cobalt allyl derivatives.[3] Studies on the polymerization of butadiene by π-allyl derivatives of Ni have been recently reported by some Russian authors.[4]

In this communication we report some results of our work on the polymerization of butadiene by π-allyl-Ni-X (X = I, Br, Cl), and also by catalysts obtained by reacting, in benzene, π-allyl-Ni-Br with, respectively, $AlBr_3$, BF_3, equimolar amounts of $AlBr_3$ and $Al(O\text{-}i\text{-}C_3H_7)_3$, equimolar amounts of BF_3 and $B(OCH_3)_3$, $TiCl_2(O\text{-}n\text{-}C_4H_9)_2$.

Our main consideration in this paper will be the stereospecificity of the polymerization process. Other aspects of the polymerization will be examined in following papers.

Experimental Studies

Materials. π-Allyl-Ni-halides were prepared from $Ni(CO)_4$ and allyl halides according to the method of Fischer.[5] The products were purified either by crystallization from pentane at low temperature or by sublimation.

Benzene, *n*-pentane, tetrahydrofuran (THF), dioxane, cyclohexanol, anisol, and ethyl alcohol, used as polymerization solvents, were pure anhydrous products.

$AlBr_3$, $TiCl_4$, $Al(O\text{-}i\text{-}C_3H_7)_3$, BF_3, $B(OCH_3)_3$, and $Ti(O\text{-}n\text{-}C_4H_9)_4$ were commercial products which were either sublimed or distilled immediately before use. The $Al(O\text{-}i\text{-}C_3H_7)_3$ used was the trimeric liquid product.[6]

Butadiene was 99% pure (Phillips, pure grade).

Polymerization. Polymerization runs were performed in cylindrical glass reactors of 50 cc. capacity, having a central neck and a side arm, which was connected with a vacuum-nitrogen apparatus, in order to remove the air from the reactor and to introduce anhydrous N_2. Anhydrous butadiene was added to the red solution of π-allyl-Ni-halide and the resulting solution allowed to stand at 18°C. in a thermostated bath, with occasional shaking. The polymerizations were terminated by CH_3OH containing aqueous HCl. The polymers were coagulated with CH_3OH, thoroughly washed with CH_3OH, then dried under vacuum at room temperature. In order to isolate the low oligomers, the liquid from which the solid polymers were precipitated was distilled under vacuum (water pump) with a rectifying column. The oily residue obtained after all the CH_3OH and the polymerization solvent were distilled off was dissolved in a small amount of diethyl ether, the ether solution washed with aqueous HCl, then dried over $MgSO_4$. The ether was then distilled off to obtain the pure oligomers as residue.

The polymerizations by catalysts prepared in benzene from π-allyl-Ni-Br and either $AlBr_3$, $AlBr_3 + Al(O\text{-}i\text{-}C_3H_7)_3$, BF_3, or $BF_3 + B(OCH_3)_3$ were performed as follows. The benzene solution of the cocatalyst was added to the benzene solution of π-allyl-Ni-Br. Then, after a few minutes, the monomer was added. When the cocatalyst was $AlBr_3$ or BF_3 a precipitate formed, red in the case of $AlBr_3$, brown-red in the case of BF_3. In the other cases the precipitate was practically absent, while the solution assumed a red-brown color, more or less intense depending on the cocatalyst used.

Physical Examination of the Polymers. For the x-ray examination a Norelco diffraction apparatus equipped with a Geiger counter was used. IR examination was done with a Perkin-Elmer 221 double-beam spectrophotometer supplied with NaCl optics. The polymers were examined as solution in CS_2 or as films obtained by evaporating CS_2 solutions of the polymers on a NaCl disk. The insoluble polymers were examined as films obtained by hot-pressing. The method of analysis is that reported by Morero et al.[7] The molecular weight was determined by the Machrolab vapor pressure osmometer in benzene solution. The melting temperatures were determined with the aid of a Leitz polarizing microscope.

Reaction Between π-Allyl-Ni-Br and $AlBr_3$. *A.* A solution containing 1.3 g. of $AlBr_3$ in 25 cc. of benzene was added slowly, under stirring, to a solution containing 0.9 g. of π-allyl-Ni-Br in 30 cc. of benzene (Al/Ni molar ratio about 0.9). A red oil formed, which was repeatedly washed by decantation with 10 cc. anhydrous benzene each time. When the oil was poured in *n*-pentane, it precipitated as a microcrystalline powder (I) (2.4 g.). This was repeatedly washed with pentane, then filtered and dried under vacuum at room temperature. The microcrystalline powder is sensitive to oxygen and humidity, and all the operations were performed under anhydrous N_2.

ANAL.: Calc. for $NiAlBr_4C_9H_{11}$: Al, 5.15%; Ni, 11.19%; Br, 60.95%; C, 20.61%; H, 2.1%. Found; Al, 4.8%; Ni, 10.73%; Br, 61.59%; C, 21%; H, 1.8%.

The crystalline complex I is decomposed by H_2O or CH_3OH. Benzene is present in the decomposition products. The quantitative determination of benzene was made by suspending 0.524 g. of I in 1 cc. of chromatographically pure *n*-heptane, then adding 2 cc. of H_2O to the suspension while cooling. The mixture was shaken and the two layers separated. The aqueous layer was again extracted with 0.5 cc. of *n*-heptane, which were then added to the main portion. Chromatographic analysis indicated that 78 mg. of benzene were present in the combined *n*-heptane extracts. Propylene and 1,5-hexadiene were also present.

B. A solution containing 2.7 g. of $AlBr_3$ in 50 cc. of benzene was added, dropwise with stirring, to a solution containing 0.9 g. of π-allyl-Ni-Br in 30 cc. of benzene. A red oil immediately formed, which was repeatedly washed with 15 cc. of benzene each time, then poured in *n*-heptane. The oil showed much less tendency to crystallize than that prepared as described under section *A*.

ANAL.: Calc. for $NiAl_2Br_7H_{11}$: Al, 6.82%; Ni, 7.42%; Br, 70.70%; C, 13.66%; H, 1.39%. Found: Al, 7%; Ni, 7%; Br, 68.5%; C, 14%; H, 1.1%.

0.791 g. of the complex, suspended in *n*-heptane and treated with H_2O, as described under section *A*, gave 78 mg. of benzene.

C. 2.7 g. of $AlBr_3$, dissolved in 20 cc. of benzene, were added, at room temperature and under stirring, to a benzene solution (30 cc.) containing 2 g. of hexamethylbenzene and 0.9 g. of π-allyl-Ni-Br. A red oil immediately formed, which, after repeated washings with benzene, was caused to crystallize by treatment with *n*-heptane.

ANAL.: Calc. for $NiAl_2Br_7C_{15}H_{23}$: Al, 6.17%; Ni, 6.11%; Br, 63.93%; C, 20.59%; H, 2.63%. Found: Al, 6.6%; Ni, 5.8%; Br, 63%; C, 20.0%; H, 2.4%.

0.875 g. of the red crystalline complex were suspended in 5 cc. of diethyl ether, and the suspension treated with 3 cc. of H_2O. After separation, the aqueous layer was again extracted with ether and the combined ether extracts dried over $MgSO_4$. After filtration and distillation of the ether, 0.15 g. of a white powder, m.p. ~166°C., was obtained as a residue. This substance had an IR spectrum identical with that of hexamethylbenzene and its m.p. was not depressed by addition of pure hexamethylbenzene.

Polymerization Results

π-Allyl-Ni-I gave (Table I), in all of the solvents used (benzene, *n*-pentane, THF, dioxane, diethylether, ethanol), polymers with a *trans*-1,4 structure. The crude polymerization products consisted of solid polymers, crystalline by x-ray examination, and oily products, soluble in CH_3OH. $\bar{M}_n$ was 1500–2000 for the polymers obtained in ethyl ether and about 3800 for those obtained in the other solvents. The oily products were a mixture of oligomers. A typical IR analysis of the solid polymers is as follows: *trans* double bonds 95–97%, vinyl groups 3–5%. In the oily products the percentage of vinyl groups was higher, 10–20%. It is interesting that when π-crotyl-Ni-I was used instead of the π-allyl-Ni-I, the vinyl groups in the polymers were very few. Evidently the vinyl groups, both in the solid and oily polymers obtained by π-allyl-Ni-I, can be mostly attributed to the allyl groups present at the end of the chains.

In THF, dioxane, cyclohexanol, or anisole, π-allyl-Ni-Br gave polymers with a *trans*-1,4 structure, solid crystalline polymers and oily products being simultaneously present in the polymerization products (Table II). The molecular weight of the solid polymers was generally lower than that of the polymers obtained by π-allyl-Ni-I in the corresponding solvents. In benzene, polymers nearly exclusively *trans*-1,4 were obtained in some runs, while in others, polymers predominantly *trans*-1,4, but containing also *cis*-1,4 units (about 40%), were obtained. The reasons for this difference in the results of the various runs in benzene are not yet clear.*

* *Note added in proof:* It was subsequently found that the different results obtained in benzene from π-allyl-Ni-Br were due to the presence of water in the monomer used in some runs. Water, even in very small amounts, causes the formation of *trans*-1,4 polymers, while with carefully dehydrated solvent and monomer polymers having about 60% *cis*-1,4 units were obtained.

TABLE I

Polymerization of Butadiene by π-Allyl-Nickel I

					Polymer								
					Solid					Oily[a]			
								IR analysis[b]				IR analysis[b]	
No.	Allyl-Ni-iodide, moles × 10^4	Solvent, cc.		Buta-diene, g.	g.	$\bar{M}_n$	m.p.	*trans* double bonds, %	Vinyl, groups %	mg.	$\bar{M}_n$	*trans* double bonds, %	Vinyl groups, %
1	4.6	Benzene	15	3.5	1.2	3925	122	97.2	2.8	60	196	94.4	5.6
2	6.7	Ether	40	6.5	0.4	1435	92	94.6	5.4	n.d.			
3	4.7	Ether	35	8.0	0.3	2283	98	96.9	3.1	60		89.5	10.5
4	6.7	Ethanol	20	5.0	0.5		83	96.5	3.5	120		89.6	10.4
5	4.0	Dioxane	23	5.0	0.35		118	97.3	2.7	20		90	10
6	4.5	THF	35	9.0	3.25	3710	120	95.5	4.5	n.d.			
7	3.1	Pentane	60	10.0	10.4			93.0	7.0	n.d.			
8[c]	4.0	Benzene	15	6.8	1.0			99.0	1.0	30		95	5

[a] Soluble in CH_3OH.

[b] *cis*-Double bonds (band at 13.5 μ) were found to be almost completely absent.

[c] π-Crotyl-Ni-I was used instead of the allyl derivative.

TABLE II

Polymerization of Butadiene by π-Allyl-Nickel-X (X = Br, Cl)

				Solid polymer[a]					
							IR analysis		
No.	π-Allyl-Ni-X, moles × 10^4	Solvent, cc.	Butadiene, g.	g.	$\bar{M}_n$	M.p., °C.	*trans* double, %	*cis* double, %	Vinyl groups, %
	X = Br								
1	1.4	Benzene 30	10	0.15	872	53	88.5		11.5
2	9.0	Benzene 20	6.8	0.1		70	90		10
3	10.0	Benzene 20	8	1			56	40	4
4	8.0	THF 15	6.5	0.7	±1197	99	94		6
5	12.0	Ethanol 40	7	0.2	1250	93	96.5		3.5
6	5.5	Dioxane 20	3	0.37	1680		97.5		2.5
7	8.4	Anisol 30	10	0.2			93.5		6.5
8	3.7	Cyclohexanol 15	2	0.3	1545		98		2
9[b]	6	Benzene 15	7	0.2			99		1
	X = Cl								
10	15	Benzene 15	6.8	0.1			7.7	89	3.4
11	20	Benzene 15	13	0.8			15.2	81	3.8
12	15	THF	7	0.1			90		10

[a] Oily products, soluble in CH_3OH, were present in the polymerization product, but were not examined.

[b] π-Crotyl-Ni-Br was used instead of the allyl derivative.

TABLE III

Polymerization of Butadiene by Catalysts Prepared from π-Allyl-Ni-Br and Compounds of Al, B, and Ti, Respectively[a]

No.	π-Allyl-Ni-Br, moles × 10^4	Cocatalyst, moles × 10^3		Butadiene, g.	Polymer[b]			
						IR analysis, %		
					g.	*trans*-1,4	*cis*-1,4	1,2
1	2.2	$AlBr_3$	0.2	6.5	0.5[c]	11.5	84	4.5
2	5.5	$AlBr_3$	1.0	7	1.0[c]	13	83.5	3.5
3	2.2	$Al_2Br_3(O\text{-}i\text{-}C_3H_7)_3$	2.5	4	0.8	8	88.5	3.5
4	1.0	$Al_2Br_3(O\text{-}i\text{-}C_3H_7)_3$	9	6.5	0.5	9	88	3
5	4.5	BF_3	4	4	0.6[c]	10	86	4
6	10	$TiCl_2(O\text{-}n\text{-}C_4H_9)_2$	10	8	0.2	9.5	87	3.5

[a] Polymerization temperature 18°C.; polymerization time for runs 1, 2, and 5, 10 hr.; other runs, 75 hr.

[b] Only the solid polymers have been considered. Oily polymers, however, are also present in the polymerization product.

[c] Only the polymers soluble in benzene have been considered.

π-Allyl-Ni-Cl was used so far only in benzene and THF (Table II). The polymer yield was generally much lower than for the other allyl nickel halides. In benzene, the chloride gave, under the conditions used, solid polymers that are predominantly *cis*-1,4 (about 85%) and oily products. In THF, on the other hand, π-allyl-Ni-chloride gave mainly oily products predominantly composed of *trans*-1,4 units. These oligomers are now under examination.

In some polymerization runs, the π-allyl-Ni-Br or π-allyl-Ni-I were prepared *in situ*, by introducing $CH_2{=}CH{-}CH_2Br$ or $CH_2{=}CH{-}CH_2{-}I$ into a benzene solution of butadiene and $Ni(CO)_4$, at room temperature. The polymers obtained had a predominantly *trans*-1,4 structure, but their IR spectrum showed a relatively intense band at 1750 $cm.^{-1}$, characteristic of the carbonyls of the ester groups. Another band, generally less intense, was present at 1720, and this was attributed to chetonic groups. The $>C{=}O$ groups were obviously derived from the carbon monoxide set free in the reaction of formation of π-allyl-Ni-Br, from $Ni(CO)_4$ and $CH{=}CH{-}CH_2{-}Br$.

In a series of experiments, the benzene solution of π-allyl-Ni-Br was reacted with, respectively, $AlBr_3$, equimolar mixtures of $AlBr_3$ and $Al(O\text{-}i\text{-}C_3H_7)_3$, BF_3, equimolar mixtures of BF_3 and $B(OCH_3)_3$, $TiCl_2(OC_4H_9)_2$. The products from each of these reactions, which are complexes containing Ni and Al, B, or Ti, were used as catalysts for the polymerization of butadiene. The products of the reaction between π-allyl-Ni-Br and $AlBr_3$ or BF_3 are insoluble in benzene (a red oil in the case of $AlBr_3$, a red-brown powder in the case of BF_3), and the suspension was used as catalyst. The other compounds gave on reaction with π-allyl-Ni-Br products completely soluble in benzene or containing only negligible amounts of precipitate.

The results of the polymerizations by these catalysts (Table III) can be summarized as follows:

1. The suspension obtained from π-allyl-Ni-Br and $AlBr_3$ or BF_3 rapidly polymerized butadiene, giving a product which appears to be a mixture of an insoluble fraction (mainly *trans*-1,4, but crosslinked and amorphous by x-ray) and a soluble fraction, which was predominantly *cis*-1,4 (from 75 to 85%). The insoluble polymer was certainly of cationic origin, as demonstrated by the fact that it was identical, on IR examination, with that obtained by $AlBr_3$ alone.

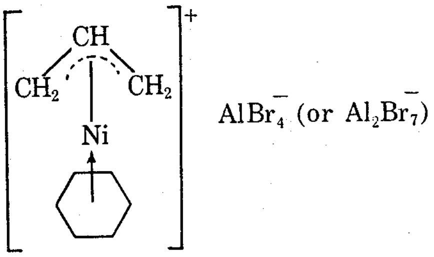
2. The homogeneous catalysts obtained from π-allyl-Ni-Br and, respectively, equivalent mixtures of $AlBr_3$ and $Al(O\text{-}i\text{-}C_3H_7)_3$, or BF_3 and $B(OCH_3)_3$, gave polymers which were soluble in benzene and were predominantly *cis*-1,4 (about 85%).

Reaction Between π-Allyl-Ni-Br and $AlBr_3$

Before discussing the polymerization results, we wish to examine briefly the reaction between π-allyl-Ni-Br and $AlBr_3$. As mentioned above (see Experimental Studies) crystalline complexes, insoluble in benzene, of composition $NiAlBr_4C_9H_{11}$ (I) or $NiAl_2Br_7C_9H_{11}$ (II), are obtained from this reaction. The insolubility in benzene seems to indicate that the complexes have an ionic character. Alcohols or water decompose them—benzene, propylene, and also some diallyl, being present in the decomposition products. Quantitative determinations for the benzene indicate that it is present in the complex in a molar ratio 1:1 with respect to Ni. The little amount of diallyl evidently arises from a coupling reaction of allyl radicals evolved in the decomposition reaction.

If the reaction between π-allyl-Ni-Br and $AlBr_3$ is performed in benzene saturated with hexamethylbenzene (the latter, being a solid with m.p. 166°C., cannot be used by itself as a solvent), complexes are obtained containing hexamethylbenzene instead of benzene. This is due to the much higher electron donating power of hexamethylbenzene with respect to benzene.

The analyses and properties of I and II agree with the formula



The $AlBr_3$ removes a σ-bonded bromine from Ni, thus creating a coordination gap, which is then filled by the π-coordination of the arene. Reactions that are analogous to that of π-allyl-Ni-Br with $AlBr_3$ have already been reported.[8]

Attempts to obtain salts of $[\pi\text{-allyl-Ni-}C_6H_6]^+$ or $[\pi\text{-allyl-Ni-}C_6(CH_3)_6]^+$ with anions such as $B(C_6H_5)_4^-$, PF_6^-, $PtCl_6^{-2}$ failed, because of the instability, in H_2O or hydroxylated solvents, of the products obtained.

Discussion of Results

Nature of the Polymerization. Any interpretation of the mechanism of polymerization by π-allyl-Ni-halides should take into consideration, in addition to what is reported here, also the results concerning the polymerization of cycloolefins such as cyclobutene and norbornene, previously reported.[2] We may recall here that these two monomers are rapidly polymerized by π-allyl-Ni-halides, in solvents such as benzene, dioxane, THF, or ethanol, to saturated polymers constituted of cyclic units. Both in the polymers of cyclobutene and norbornene, vinyl groups are present if π-allyl-Ni-X was used as catalyst.

All the results so far known of the polymerization of butadiene, cyclobutene and norbornene indicate that the propagation by π-allyl-nickel derivatives occurs by insertion of the monomer on the polarized bond between Ni and the last polymerized unit.

In particular, the following facts and considerations support this assumption.

1. The presence of vinyl groups in the polymers obtained by π-allyl-Ni-X (X = I, Br, Cl), and the much lower amount of them in polymers obtained by π-crotyl-Ni-X shows that the first monomeric unit is incorporated on the bond between Ni and the allyl or crotyl group.

2. The presence of ester groups in polybutadienes obtained by reacting *in situ* $Ni(CO)_4$ and $CH_2{=}CH{-}CH_2X$ is easily explained if we assume that the bond between Ni and the last polymerized unit is of the π-allylic type. It is known,[9] in fact, that carbon monoxide reacts with π-allyl-Ni-X to give eventually, if an alcohol is present, esters of vinylacetic acid. It has been shown[10] that the reaction occurs through the intermediate $CH_2{=}CH{-}CH_2{-}CO{-}NiX$. In our case the formation of ester groups evidently occurs in the same way. The only difference is that, instead of having an allyl group bonded to Ni, we have the polybutadiene chain.

3. The following facts eliminate the possibility that the polymerization by π-allyl-Ni-X is of pure radical type: (*1*) cyclobutene and norbornene are not polymerized by the usual radical initiators;[11] (*2*) the polybutadiene obtained by radical initiator has a different structure from that obtained by π-allyl-Ni-X.

4. It seems reasonable to exclude the possibility that the polymerization by π-allyl-Ni-X is of cationic type, since monomers highly sensitive to cationic catalyst (e.g., styrene, isobutene), are not polymerized by allyl-Ni-halides.

It seems reasonable to conclude that the polymerizations by allyl-Ni-derivatives is of the type we call "coordination anionic," which means that the monomer first coordinates to the transition metal and is then incorporated into the polarized metal–carbon bond between Ni and the last polymerized unit.

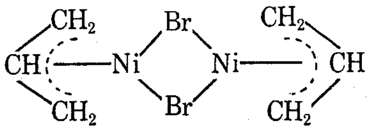
It is interesting that, according to the above results, a polymerization of this type can also be performed in hydroxilated solvents, such as ethanol, when the metal–carbon bond that is the active site in the polymerization is stable in the solvent used. This fact further supports the hypothesis that the polymerization of butadiene[12] in H_2O or alcohols, by salts of Rh, Ru, Os, is of the same type of that by π-allyl-Ni-X as far as the way of incorporation of the monomer is concerned. A π-allylic bond is probably formed in the reaction between butadiene and the salts of Rh, Ru, Os. In the recent literature, reactions between butadiene and salts of Ru, Rh, with formation of π-allylic bonds have already been reported.[13]

The above considerations apply to the polymerization by π-allyl-Ni-X. It seems, however, that also in the case of the catalysts obtained from π-allyl-Ni-Br and $AlBr_3$, BF_3, etc., the polymer grows by insertion on a Ni—C bond. This seems supported by the following facts. The polybutadienes obtained by these bimetallic catalysts contain a higher proportion of vinyl groups when they are prepared from π-allyl-Ni-Br rather than when from π-crotyl-Ni-Br. Analogously, the polymers of cyclobutene or norbornene obtained by these bimetallic catalysts contain vinyl or crotyl groups, depending on the nickel derivative used. Furthermore, the considerations set forth in sections *3* and *4* lead to exclude that the systems obtained from π-allyl-Ni-Br and compounds of Al, B, or Ti polymerize by a cationic or radical mechanism.

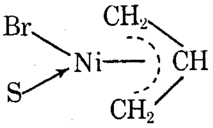
The most probable hypothesis, therefore, remains that also in the case of these bimetallic catalysts, the polymer chain grows through the following steps: (*1*) coordination of the monomer to Ni; (*2*) incorporation of the coordinated monomer into the Ni—C bond.

Stereospecificity of the Polymerization. Crystalline *trans*-1,4 polymers or predominantly *cis*-1,4 polymers can be obtained with π-allyl-Ni-X or systems containing it, as discussed above. The causes of the different stereospecificity are difficult to explain. We try in the following to give a tentative interpretation of some of the facts observed.

π-Allyl-Ni-I and π-allyl-Ni-Br are dimeric in benzene solution, with 4-coordination around Ni:



In THF, dioxane, and alcohol most probably they are monomeric, because these solvents split the halogen bridges. Since, however, they coordinate to Ni, the coordination around the latter in these solvents should remain the same as in benzene:



(S = solvent, i.e., THF, dioxane, etc.)

In this situation, butadiene would coordinate to Ni only through one vinyl group, and then would be incorporated as *trans*-1,4 unit. The *trans* configuration of the double bond in the monomeric unit arises from the fact that, at room temperature, butadiene monomer is in the *trans* conformation.

When π-allyl-Ni-Br is reacted with $AlBr_3$, or each of the other compounds mentioned above, the cation $[\pi\text{-}C_6H_6\text{-Ni-}\pi\text{-}C_3H_5]^+$ forms. In this case butadiene can coordinate to Ni by the two double bonds, in the *cis* conformation and, therefore, would be incorporated as *cis*-1,4 unit. The coordination of the monomer to the above cation occurs, obviously, by displacing the arene.

The fact that π-allyl-Ni-Cl gives in benzene polymers containing a large proportion of *cis*-1,4 units could be explained as follows. The chloro-bridges between the atoms of Ni in the dimeric compound are less resistant to fission by nucleophilic reagents than the bromo- or iodo-bridges. Therefore, they could be split also by a weak nucleophilic reagent such as butadiene, with consequent formation of the monomeric species $\pi\text{-}C_3H_5\text{-Ni-Br}$. Butadiene can coordinate to such a species by the two double bonds, in the *cis* conformation, before its incorporation into the growing chain. Consequently *cis*-1,4 units would be formed in this case.

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Résumé

Le butadiène a été polymérisé avec l'halogénure de nickel-π-allylique (I) pour former des polymères stéréoréguliers de faibles poids moléculaires, utilisant comme solvant, soit le benzène, le pentane normal, le tétrahydrofurane, le cyclohexanol ou l'alcool éthylique. Les polymères solides et des produits huileux ont été obtenus simultanément comme produits de polymérisation. Dans le benzène comme solvant, le π-allyl-Ni-I et le π-allyl-Ni-Br fournissaient surtout des polymères *trans*-1,4 tandis que le π-allyl-Ni-Cl fournit des polymères principalement composés d'unités *cis*-1,4. Dans les autres solvants, on obtient surtout des polymères *trans*-1,4 indépendamment du dérivé du nickel utilisé. En faisant réagit le π-allyl-Ni-Br, en solution dans le benzène avec $AlBr_3$, $Al_2(O\text{-}i\text{-}C_3H_7)_3Br_3$, BF_3, ou $TiCl_2(O\text{-}i\text{-}C_3H_7)_2$, on obtient des complexes (II) qui polymérisent le butadiène en polymères *cis*-1,4. On montre que ces complexes sont du type ionique et contiennent le cation (voir la structure dans le texte anglais). La différente stéréospécificité observée dans les polymérisations par I et par II est interprétée sur la base du mode différent de coordination du butadiène au Ni dans les complexes I et II respectivement.

Zusammenfassung

Butadien wurde in Benzol, *n*-Pentan, Tetrahydrofuran, Cyclohexanol oder Äthylalkohol als Lösungsmittel mit π-Allyl-Ni-halogeniden (I) zu niedermolekularen stereoregulären Polymeren polymerisiert. Als Polymerisationsprodukte wurden gleichzeitig feste Polymere und ölige Produkte erhalten. In Benzol als Lösungsmittel lieferten π-

Allyl-Ni-I und π-allyl-Ni-Br vorwiegend *trans*-1,4-Polymere, während π-Allyl-Ni-Cl zu grösstenteils aus *cis*-1,4-Einheiten bestehenden Polymeren führte. In den anderen Lösungsmitteln wurden unabhängig vom verwendeten Nickelderivat vorwiegend *trans*-1,4-Polymere erhalten. Durch Reduktion von π-Allyl-Ni-Br in Benzollösung mit $AlBr_3$, $Al_2(O\text{-}i\text{-}C_3H_7)_3Br_3$, BF_3 oder $TiCl_2(O\text{-}i\text{-}C_3H_7)_2$ wurden Komplexe (II) erhalten, welche Butadien vorwiegend in *cis*-1,4-Polymere umwandeln. Es wird gezeigt, dass es sich um ionische Komplexe mit dem Kation (Bzgl. Struktur vgl. englische Zusammenfassung) handelt. Die bei der Polymerisation mit I und II beobachtete verschiedenartige Stereospezifität wird auf eine verschiedenartige Koordination von Butadien an Ni in den Komplexen I und II zurückgeführt.