

Polymerization of Propadiene. I. Comparison of Catalytic Systems in Relation to Polymer Structure and Polymerization by a New Ni-Based Catalyst

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Synopsis

A literature survey is given of the methods of preparation of 1,2- and 1,2,2,1-polyallene. The spectroscopic data and other physico-chemical properties are compiled. Spectral analysis of the products in relation to the catalyst used leads to conclusions with regard to the effect of electron-donating and electron-withdrawing ligands to the transition metal of the catalyst on the ratio of 1,2 to 1,2,2,1-polyallene structural units in the polymer obtained. This hypothesis enabled us to prepare a structurally homogeneous 1,2 polyallene in almost quantitative yield. The catalyst was prepared by adding propadiene to a benzene solution of Ni(II) acetylacetonate followed by addition of triisobutylaluminum. This sequence of addition appeared to be the essential factor for obtaining an active catalyst. A kinetic scheme for the polymerization is put forward.

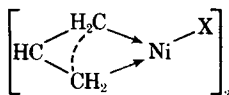
INTRODUCTION

Propadiene can be polymerized by several catalysts. Baker,¹ Robinson,² and Havinga³ used various Ziegler-type catalysts.

Baker obtained a high molecular weight, linear polyallene which was either amorphous or crystalline, depending on the reaction conditions. The product, however, was structurally homogeneous and consisted of blocks of vinylidene, vinyl, and *cis*-olefin units. A selective anionic attack on the terminal carbon atom of propadiene was proposed to explain this structure.

Havinga³ obtained a product in which the unit $-\text{CH}_2-\overset{\text{H}_2\text{C}}{\text{C}}=\text{CH}_2$ was predominant. The high degree of crystallinity led him to suppose that only small structural irregularities were present.

In 1965 Otsuka et al.⁴ reported the preparation of polyallene by means of the catalyst bis- π -allyl Ni-halide:



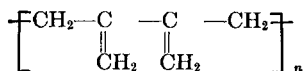
where X may be Cl, Br, or I. In this case structurally nearly homogeneous 1,2 polyallene was claimed.

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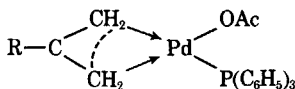
Later Otsuka et al.⁵ reported the preparation of 1,2 polyallene by using a Rh catalyst which was prepared from dicarbonyl Rh(I) μ -dichlorodicarbonyl-Rh(I) $(\text{Rh}(\text{CO})_2\text{Cl})_2$, and triphenylphosphine $\text{P}(\text{C}_6\text{H}_5)_3$ in ethanol. No structure for the catalyst was given.

Shier⁶ published the preparation of 1,2,2,1-polyallene



in an acetic acid solution of $\text{Pd}(\text{NO}_3)_2$ and triphenylphosphine and a small amount of *p*-toluenesulfonic acid.

He proposed a π -allyl Pd-complex as the active catalyst:



but did not isolate this.

Without the addition of $\text{P}(\text{C}_6\text{H}_5)_3$, 80 of the converted allene is accounted for by a mixture of dimeric structures, originating from the addition of one or two molecules of solvent to one or two moles of propadiene.

Until now other catalyst systems have not been very successful. Reactions of allene with dicobalt octacarbonyl⁷ or nickel(II) acetylacetonate and triethylaluminum⁸ are reported to yield insoluble polymers of unknown structure.

We have verified the work of Shier⁶ and, in part the work of Otsuka^{4,5} with slight modifications.

Our data, together with those collected from the literature, with respect to catalyst systems, infrared absorptions of various types of polymer, and physical properties are given below in the tables.

In the literature no explanation is offered for the fact that the catalysts used are specific for a defined structure of the polymer. It was found by Otsuka⁸ that, on polymerizing propadiene by means of π -allyl Ni-halide complexes, the proportion of 1,2,2,1 polymer structure increases in the following order: $\text{I} > \text{Br} > \text{Cl}$, the ratios 1,2/1,2,2,1 being, respectively, 79/21 for I, 87/13 for Br, and 90/10 for Cl. This indicates that ligands with a strong electron-withdrawing effect (due to a greater π - $d\pi$ overlap) give rise to a greater part of the 1,2,2,1 structural element in the polymer.

We thus conclude that, in analogy with the Ziegler-Natta catalysts, alkylation of the central transition metal atom, that is, introduction of an electron-donating ligand, leads to the formation of a catalyst which polymerizes propadiene to a structure which contains more or only 1,2,1,2 units.

The electrondensity on the central metal atom depends on the type of metal and the type of ligand to the metal.

In this publication we describe an alkylated Ni-based catalyst system which polymerizes propadiene exclusively to 1,2-polyallene. Alkyl is introduced here as the electron-donating ligand. This result confirms our hypotheses.

EXPERIMENTAL

Materials

Propadiene was obtained from J. T. Baker Chemicals and dried before use with molecular sieves and a solution of triethyl aluminum in hexane. Benzene and other solvents were degassed and purified by distillation in an inert atmosphere and dried carefully before use.

Infrared Spectra

All infrared spectra were recorded on a Unicam S.P. 500 spectrometer.

Melting Points

Melting points were determined on a Dupont D.T.A. apparatus.

Preparation of 1,2,1,2-Polyallene

The procedure described by Otsuka⁵ was modified but with the same catalyst component and the same concentration. The polymerization was carried out at 40°C under 4 atm of propadiene pressure. The yield was almost-quantitative.

Preparation of 1,2,1,2-Polyallene with Ni(acac)₂ + TiBA as the Catalyst

Ni(II) acetylacetonate (0.02 mmole) was dissolved under a nitrogen atmosphere in 50 ml dry, degassed benzene. The benzene was saturated with dried propadiene while stirring. No polymerization is observed at this stage of the reaction. A solution of triisobutylaluminum (1 mole/l.) is then added dropwise until an Al/Ni ratio of 10 is reached. Propadiene is bubbled through continuously. Polymerization starts at a ratio Al/Ni = 2.

TABLE I
Physical Properties of Different Types of Polyallene

	Polymer I	Polymer II	Polymer III	Remarks
Solubility	C ₆ H ₅ Cl, C ₆ H ₅ CH ₃ , C ₆ H ₄ (CH ₃) ₂ (boiling)	Common hydrocarbons (room temp)	Benzene (boiling)	
Melting point, °C	120-130	42	62	
\bar{M}_n	50,000	4000	10 ⁶	
Reaction with maleic anhydride	Negative	Positive	Positive	In a positive reaction the 1600 cm ⁻¹ absorption disappears and the 1635 cm ⁻¹ absorption increases in intensity (Table III)

The color of the reaction mixture changes from light yellow to red and polymer starts to precipitate at the moment of color change. The reaction mixture is allowed to stir for 30 min.

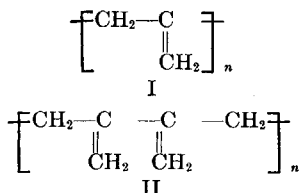
The product is isolated with a methanol/HCl mixture (20/1), filtered, and dried *in vacuo* for 24 hr; the yield is 750 mg.

Properties of the Isomeric Polyallenes

Table I summarizes the properties of the various types of polyallene.

RESULTS AND DISCUSSION

Propadiene can polymerize into two different structures: viz. 1,2,1,2-polyallene (I) and 1,2,2,1-polyallene (II).



It is seen from Table II that the polymer structure strongly depends on the catalyst used. The low valent π -allyl-Ni complexes give rise to a structurally mixed polymer (III).^{4,9}

Starting from our hypothesis put forward in the introduction, we have investigated the activity of the system nickel (II)-acetylacetonate and triisobutylaluminum. When these two reagents are brought together in a benzene solution at room temperature, an immediate reduction of Ni(II) \rightarrow Ni(O) occurs, and the system is inactive for polymerization of propadiene.

If, however, Ni (II) acetylacetonate is dissolved in benzene and this solution is saturated with propadiene, addition of triisobutylaluminum leads to the formation of a red solution which is very active for the polymerization of propadiene.*

TABLE II
Various Catalysts for the Preparation of Polyallene^a

Polymer type I	Ref.	Polymer type II	Ref.	Polymer type III	Ref.
VOCl ₃ -TEA ^a	1, 3	Pd(NO ₃) ₂ + 2P(C ₆ H ₅) ₃ ^c	7	π C ₃ H ₅ NiX ₂	5, 9
Rh(CO) ₂ Cl ₂ + 2P(C ₆ H ₅) ₃ ^b	5			(π C ₈ H ₁₂) ₂ Ni	5, 9
TiCl ₄ -TiBA ^a	2			π C ₃ H ₅) ₂ Ni	5, 9
FeBr ₃ -TiBA	2			π C ₃ H ₅ N ₂ Ni	5, 9
VOCl ₃ -TiBA	2				

^a TEA = triethylaluminum; TiBA = triisobutylaluminum; X = Cl, Br, I.

^b In EtOH solution.

^c In acetic acid solution.

* Otsuka,⁴ using the same system, obtained in low yield (16%) an insoluble gel of polyallene.

It was found that the sequence of addition is the essential factor which governs the formation of an active complex. In this complex propadiene probably takes part as a ligand. The polymer obtained, soluble in boiling chlorobenzene, toluene, and xylene, was structurally homogeneous 1,2,1,2-polyallene according to its infrared spectrum.

Infrared Spectra of Polyallenes

In our investigation of the polymerization of propadiene, we have used the infrared spectra almost exclusively to assign the obtained structures. Table III gives the characteristic polyallene absorptions. The most characteristic absorptions for polymer identification are the 1600 cm^{-1} band and the frequency of the C—H deformational vibration of the CH_2 group.

We have observed in our experiments that polymerization occurs only if the Al/Ni ratio in the catalyst components exceeds a certain value R . This value is concentration-dependent. When $\text{Al/Ni} \leq R$, a yellow solution is obtained, which is catalytically inactive. However, no reduction to Ni(O) is observed.

When $\text{Al/Ni} > R$, the yellow solution turns red and polymerization starts immediately.

Table IV shows the results of a series of experiments, in which the Al/Ni ratio was varied, while the Ni concentration was kept constant.

From the above two conclusions may be drawn: (1) at $\text{Al/Ni} = 2$ the inactive yellow solution turns into a red active catalyst system; (2) Once this ratio 2 is exceeded, the polymer yield is proportional to the Al/Ni ratio.

From a second series of experiments it became clear that the Al/Ni ratio at the start of polymerization is dependent on both the aluminum and nickel concentration. The system becomes active when the product $[\text{Al}][\text{Ni}]$ $0.272\text{ mole}^2/\text{l.}^2$. This is illustrated in Table V.

TABLE III
Infrared Spectra of Different Types of Polyallene

Vibrational type	Absorption bands, cm^{-1}		
	Polymer I	Polymer II	Polymer III
C—H stretching			
C=CH ₂	3080	3080	3080
CH ₂	2950, 2890	2950, 2890	2950, 2890
C=C stretching			
Nonconjugated	1635	—	1635
Conjugated	—	1640	1640
	—	1600	1600
CH deformation			
CH ₂ (I)	1435	—	1435
CH ₂ (II)	—	1465	1465
C=CH ₂	900	900	900
Overtone	1800	1800	1800

TABLE IV
Polymer Yield in Relation to the Al/Ni Ratio (22°C, 50 ml benzene)

[Ni], mmole/ 50 ml	[Al/Ni] mmole/ mmole	[C ₃ H ₄], mmole/ 50 ml ^a	Time, hr	PA, mmole C ₃ H ₄	Conversion, %	[Al] - 2[Ni] mmole
0.103	1.0	37.5	17	0	0	
0.0985	1.5	37.5	17	0	0	
0.0918	2.0	37.5	17	0.023	0.06	0
0.085	2.3	37.5	17	0.665	1.77	0.026
0.107	2.7	37.5	17	2.49	9.0	0.074
0.097	3.0	37.5	17	2.26	6.0	0.097
0.100	3.5	37.5	17	5.17	14.0	0.150
0.114	6.0	37.5	17	9.90	36.0	0.456

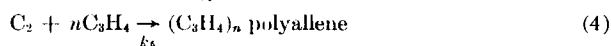
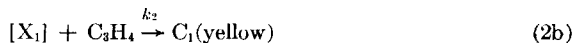
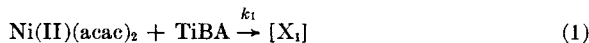
^a During the polymerization reactions no further monomer was supplied.

TABLE V
Minimum Value of Al/Ni for Start of Polymerization

[Ni], mmole	[TiBA], mmole	[Al/Ni], mole/ mole	Vol. ml	$\frac{[Al]}{1}$	$\frac{[Ni]}{1}$	[Al] · [Ni]
0.02	0.320	16	150	2.13	0.133	0.283
0.02	0.123	6.2	100	1.23	0.20	0.246
0.02	0.036	2.0	50	0.72	0.90	0.288
Avg.						0.272

The polymerization gives the best results, if, at high Al/Ni ratio,⁶ in a concentrated solution (± 0.5 mmole Ni/l.), monomer is supplied during the reaction. For example, a ratio polymer/Ni = 960 was obtained in 20 min when a ratio Al/Ni = 10 was used ([Ni] = 0.3 mmole/l.).

The following experimental facts, lead us to a hypothesis for the kinetics of this reaction, in which the existence of an equilibrium is essential: no reduction Ni(II) \rightarrow Ni(O) by triisobutylaluminum (TiBA) in the presence of propadiene; the observed start of polymerization at the point of color change from yellow to red; the necessity for a minimum value of the product [Al][Ni] for polymerization activity; the dependence of the activity on the Al/Ni ratio. The proposed mechanism is given in eqs. (1)–(4).



Reaction (1) seems necessary, while a termolecular reaction



seems hardly feasible.

In the presence of propadiene, reaction(2b) takes place and reduction to Ni(O) [reaction (2a)] is avoided.

Thus propadiene appears to be a stabilizing ligand, which makes the formation of C_1 possible. The complex C_1 is not active for polymerization. We suppose that alkylation by the aluminum alkyl takes place and the complex C_2 is formed. From the facts mentioned above we conclude the existence of an equilibrium. We have isolated the complexes C_1 and C_2 . Due to purification difficulties no satisfactory analytical results were obtained.

Properties of the Prepared Polyallene

Infrared spectroscopy showed that the polymer had the 1,2,1,2 structure¹ (Table VI).

TABLE VI
Infrared Spectrum of Polyallene Obtained from Ni(II)acac + C_3H_4 + TiBA

Vibration type	Absorption bands, cm^{-1}
CH stretching	
C=CH ₂	3080
/	2950
CH ₂	2890
\	
C=C stretching	
Nonconjugated	1635
Conjugated	—
CH deformation	
CH ₂	1435
/	
C=CH ₂	900
\	
overtone	1800

The other properties of the polymer are also in accord with the proposed structure. It is soluble in boiling chlorobenzene,¹ toluene, and *p*-xylene. The melting range is 113–122°C. The intrinsic viscosity in chlorobenzene at 60°C [η] is 0.98.

CONCLUSION

The foregoing facts justify the conclusion that we have found a very active catalyst system for the polymerization of propadiene, based on Ni and the stabilizing ligand propadiene.

It seems highly probable that the electron-donating properties of the alkyl ligand, as in Ziegler-Natta catalysts,¹ are responsible for the exclusive formation of 1,2,1,2 polyallene. Analogous catalyst systems based on other transition metals and various stabilizing ligands and their activity towards the polymerization of propadiene as well as other monomers will be the subject of a future publication.

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