After two reprecipitations from ethanol by addition of ether it melted at 197–199°.

Anal. Calcd. for $C_{20}H_{30}IN_3O$: C, 52.74; H, 6.64; I, 27.87; N, 9.23; O, 3.51. Found: C, 52.31; H, 6.63; I, 27.71; N, 9.33; O, 3.51.

Acknowledgment.—The authors wish to acknowledge many helpful discussions with Dr. Keith McCallum of these laboratories, particularly with regard to interpretation of n.m.r. spectra.

The Polymerization of Acetylenes by Nickel Halide–Tertiary Phosphine Complexes

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Received March 3, 1964

The polymerization of several acetylenic compounds by nickel complexes of the type $NiX_2 \cdot 2R_3P$ is described. Acetylene and phenylacetylene are polymerized chiefly to the linear *trans* polyenes. Propynol gives equal amounts of linear polymer and aromatic trimers. The catalytic efficiency increases in the series: $NiCl_2 \cdot 2R_3P$, $NiBr_2 \cdot 2R_3P$, and $NiI_2 \cdot 2R_3P$.

The polymerization of acetylene to a high molecular weight linear polyene of predominantly *trans* structure was first described by Natta.[1] More recent publications of Greene,[2] Luttinger,[3] and Luttinger and Colthup[4] have shown that reducing agents such as sodium borohydride react with group VIII metal salts or complexes such as $NiCl_2 \cdot 2Bu_3P$ to form catalytic species which polymerize acetylene to the same polymer described by Natta.

We wish to report that nickel halide–tertiary phosphine complexes themselves are catalysts for the polymerization of acetylene, phenylacetylene, 1-hexyne, and propargyl alcohol. The catalytic activity is apparently specific for nickel–phosphine complexes, cobalt and palladium complexes being completely inactive, as was a nickel–phosphine oxide complex.

Bis(triphenylphosphine)nickel chloride was not a very active catalyst, while both bis(triphenylphosphine)nickel bromide and bis(tri-*n*-butylphosphine)-nickel bromide were good catalysts, as was bis(triphenylphosphine)nickel iodide.

The polymerization of acetylene leads to a black, insoluble solid whose infrared spectrum and X-ray diffraction pattern agreed with the data of Natta[1] and Luttinger[3] for polyacetylene.

The polymerization took place in a variety of solvents such as ethanol, tetrahydrofuran (THF), benzene, and acetonitrile. Dangerous exotherms were frequently observed when THF was used, but not with ethanol. In addition, the yield (grams of polymer/gram of catalysts) was increased about twofold on changing from THF to ethanol, and a more ordered polymer, as shown by X-ray diffraction, was obtained. An optimum yield of 12.7 g. of polymer/gram of catalyst was obtained.

Phenylacetylene yielded a yellow solid as main product in small yield, the infrared spectrum of this solid was identical with that of poly(phenylacetylene).[5]

It was found that propynol yielded, in addition to isomeric trimethylolbenzenes reported by Reppe,[6] an insoluble solid whose infrared spectrum showed the main absorptions of polyacetylene and poly(phenylacetylene) in addition to bands due to $-CH_2OH$, which is very likely polypropynol, $\left[CH = C(CH_2OH)\right]_n$. Soluble and insoluble products from propynol have been reported by Polyakova, *et al.*,[7] from thermal polymerization under pressures of 1500 to 1600 atm.

Under the above conditions, 1-hexyne yielded small amounts of linear dimers, trimers, and tetramers. Ethylene, vinyl acetate, vinyl chloride, and styrene failed to polymerize either by themselves or with acetylene. This polymerization resembles the polymerization of 1,3-butadiene by salts and complexes of rhodium and other transition metals reported by Rinehart,[8] and Canale,[9] in that no apparent cocatalyst is required.

Experimental

Chemicals.—Phenylacetylene and 1-hexyne were used as received from the Farchan Research Laboratories. Matheson acetylene was used directly. Triphenylphosphine was used as received from Eastern Chemical Co. Tri-*n*-butylphosphine was used as received from Metal and Thermit Corp. Transition metal salts were reagent grade. Tetrahydrofuran, J. T. Baker reagent grade, was used as received.

Bis(triphenylphosphine)nickel dichloride, dibromide, and diiodide[10]; bis(triphenylphosphine)cobalt dichloride, dibromide, and diiodide[11]; bis(tri-*n*-butylphosphine)nickel dibromide[12] bis(tri-*n*-butylphosphine)palladium dichloride[13]; and bis(triphenylphosphine oxide)nickel dibromide[14] were prepared by known methods.

Acetylene. Procedures.—Acetylene polymerizations were carried out in a 1-l. stainless steel, stirred autoclave at prevailing temperatures. As an example, 500 ml. of solvent (10% THF–90% EtOH) containing 3.7 g. (0.005 mole) of $NiBr_2 \cdot 2Ph_3P$ was placed in the autoclave; the autoclave was closed, flushed three times with nitrogen at 100 p.s.i.g., then pressured to 70 p.s.i.g. with N_2 and a total of 200 p.s.i.g. with acetylene. The autoclave was run at these conditions for 24 hr. After venting unreacted acetylene, the contents of the autoclave were seen to be a dark reaction mixture with much black solid suspended in the solvent. After filtration, the solid was washed with fresh solvent until all color bodies were removed, dried at about 40 mm. over KOH, bottled quickly under N_2, and weighed. There was 47.0 g.

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[2] M. L. H. Greene, M. Nehme, and G. Wilkinson, *Chem. Ind.* (London), 1136 (1960).

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[7] A. M. Polyakova, V. V. Korshak, and M. D. Suchkova, *Polymer Sci.* (USSR), **4**, 164 (1962).

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[9] A. J. Canale, W. A. Hewett, T. M. Shryne, and E. A. Youngman, *Chem. Ind.* (London), 1054 (1962).

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[11] J. Chatt and B. L. Shaw, *ibid.*, 285 (1961).

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TABLE I

POLYMERIZATION OF ACETYLENE BY TRANSITION METAL HALIDE–PHOSPHINE COMPLEXES

Expt.	Catalyst	Solvent	Temp., °C.	Exotherm, °C. (hr.)	Product, g.	Yield, g. of polymer/ g. of catalyst
1	$NiBr_2$	THF	11–16	None	0	0
2	Ph_3P	THF	13–19	None	0	0
3	$NiCl_2 \cdot 2Ph_3P$	THF	12–15	None	2.1	0.63
4	$NiBr_2 \cdot 2Ph_3P$[a]	THF	10–20	10–140 (1)	23.6	6.37
5	$NiBr_2 \cdot 2Ph_3P$	10% THF 90% EtOH	16–18	None	47.0	12.70
6	$NiI_2 \cdot 2Ph_3P$	THF	21–24	22–75 (1)	20.0	4.75
7	$NiBr_2 \cdot 2(n\text{-}Bu_3P)$	THF	19–22	None	22.0	6.65
8	$NiBr_2 \cdot 2Ph_3PO$	10% THF 90% EtOH	20	None	0	0
9	$NiBr_2 \cdot 2Ph_3As$[b]	EtOH	7–16	None	0	0
10	$CoCl_2 \cdot 2Ph_3P$	THF	16–18	None	0	0
11	$CoBr_2 \cdot 2Ph_3P$	THF	70	None	0	0
12	$CoI_2 \cdot 2Ph_3P$	THF	16–20	None	0	0
13	$PdCl_2 \cdot 2(n\text{-}Bu_3P)$	THF	15–21	None	0	0

[a] This reaction also proceeded in *n*-propyl alcohol, benzene, acetone, and acetonitrile to about the same extent. [b] $NiBr_2$ and triphenylarsenic were added separately to the solvent in stoichiometric amounts.

of polyacetylene obtained or a yield of 12.7 g. of polymer/gram of catalyst.

Anal. Calcd. for $(C_2H_2)_n$: C, 92.26; H, 7.74. Found: C, 86.00; H, 7.27; ash, 5.31.

The ash content was further reduced by a methanol wash to 1.53% total ash. This sample contained 0.37% Ni, which on further treatment with anhydrous HCl in chloroform was removed to less than 0.02%. Halogen in the polymer was not removed by any of these washings, varying between 1 and 2%.

Polyacetylene samples were always characterized in the infrared (KBr disk) by the presence of strong bands (among others not identified) at 2940–2790, not assigned; 1640, due to the stretching of conjugated $-\!(CH{=}CH)\!-$ chain; 1100, vibration out of plane of *trans* ethylenic hydrogen atoms; and 699–761 cm.$^{-1}$, vibration out of plane of *cis* ethylenic hydrogens (generally quite weak). The spectra were in agreement with those reported by Natta,[1] Luttinger,[3] and Watson.[15]

Polyacetylene prepared as above gave more intense and sharper reflections on X-ray diffraction examination at Bragg angles corresponding to interplanar spacings of 3.73, 2.82, and 2.14 Å. than did polyacetylene samples prepared with Luttinger's[3] catalyst system. Also the 2.14-Å. reflection was not observed in polyacetylene prepared after Luttinger. Caution should be used in handling finely powdered polyacetylene. This form of the polymer reacts quickly with oxygen to give an oxygenated material, generally red or brown in color, which has been seen to ignite on several occasions without warning. One such instance occurred while the polymer was under a vacuum of 1 mm. The material burns fiercely and rapidly.

In evaluating a sample of polyacetylene in a Bureau of Mines impact tester, the material was found to be very sensitive, on an average of 14 cm./2 kg.[16] This material was prepared as described above, but was apparently more cross linked since it could not be powdered, showing instead obsidian fracture. It is not known with certainty why this one preparation was impact sensitive, while others were not, although variable oxygen content in commercial acetylene is suspect.

Polyacetylene prepared by Green–Luttinger catalyst system[2,3] was always obtained as a very hard, shiny plug which was difficult to pulverize. It could be fractured by sharp blows with a hammer, revealing obsidian fracture.

Polyacetylene prepared with $NiBr_2 \cdot 2Ph_3P$ *in ethanol* was, in contrast, isolated as a black, lusterless cake which was easily powdered by rubbing with the fingers. It is thought that the polyacetylene prepared with $NiBr_2 \cdot 2Ph_3P$ is less cross linked than the hard material prepared with the Green–Luttinger catalyst.

1-Hexyne.—A solution of 5.0 g. (0.007 mole) of $NiBr_2 \cdot 2Ph_3P$ in 250 ml. of THF containing 55.0 ml. (0.5 mole) of 1-hexyne (green solution) was refluxed for 14 hr. A color change to dark brown was observed at the end of this time. On removal of volatile compounds at 40 mm. on a steam bath, a residue was obtained which was a mixture of a brown viscous liquid and a green, semisolid oil. The green material was not investigated carefully but yielded nickel hydroxide on treatment with aqueous sodium hydroxide. The brown liquid was distilled through a 6-in. Vigreux at reduced pressure. A golden yellow distillate (12 g.) was obtained, b.p. 127–134° at 2 mm., n^{25}_{D} 1.4872. Merriwether[17] gave n^{25}_{D} 1.4893 for his 1-hexyne polymerisate, a mixture of linear and aromatic trimers. Our sample showed infrared bands at 1500, 1600, 707, and 850 cm.$^{-1}$ attributable to trisubstituted aromatic products.

Phenylacetylene.—A solution of 5.0 g. of $NiBr_2 \cdot 2Ph_3P$ (0.007 mole) in 125 ml. of THF (green) was refluxed with 31.0 ml. (0.26 mole) of phenylacetylene for 18 hr. A final, red-brown color was observed and a yellow solid formed. This was filtered, washed with cyclohexane, and stored. The filtrates were evaporated on a steam bath and the residue, a thick, red oil, was dissolved in chloroform. Addition of a large excess of methanol caused a yellow solid to precipitate. This was filtered, washed with cyclohexane, and dried under vacuum. On combination with the first fraction, a total of 4.7 g. was obtained.

Anal. Calcd. for $(C_8H_7)_n$: C, 93.4, H, 6.6; mol. wt., 980 (cryoscopic, benzene). Found: C, 88.66; H, 6.01; Br, 0.77; Ni, 2.6.

Its infrared spectrum was nearly identical with that of Okamoto's[5] poly(phenylacetylene), showing the major bands of the polyacetylene chain in addition to phenyl absorptions. There was isolated from the mother liquors of the above isolation a total of 25.7 g. of viscous, red-brown oils. These could not be forced to yield individual compounds by crystallization, precipitation, distillation, or sublimation. They were similar in infrared spectra to the linear poly(phenylacetylene), but had in addition strong bands due to aromatic trisubstitution.

The reaction of phenylacetylene and nickel bromide–triphenyl phosphine differs from the reaction of phenylacetylene and the Green–Luttinger system in that the former catalyst yields about 15% linear poly(phenylacetylene) while the latter gives about 60% trimers,[3] both aromatic and linear. Phenylacetylene in our system is not so active as acetylene itself.

Propynol.—A solution of 5.0 g. of $NiBr_2 \cdot 2Ph_3P$ (0.007 mole) in 350 ml. of THF (green) containing 150 ml. of propynol was heated at 100° for 24 hr. in a nitrogen-blanketed, stirred autoclave. On work-up, a rust-colored solid was isolated by filtration. After washing with fresh THF and drying to constant weight, 30.0 g. was obtained, insoluble in water and all organic solvents tried.

Anal. Calcd. for polypropynol, $(C_3H_4O)_n$: C, 64.30; H, 7.15. Found: C, 63.57; H, 6.40; Br, 0.72; Ni, 1.1; P, 0.37.

The substance absorbed in the infrared at 3300 (hydroxyl), 2850 ($-CH_2-$), conjugated $-\!(CH{=}CH)\!-$ at 1635, and had characteristic 1020-cm.$^{-1}$ band of the polyacetylene *trans* structure. This solid appears to be polypropynol of the structure $-\!(CH{=}C(CH_2OH))\!-$. There was also isolated from the filtrates 50 g. of a red, water-soluble, viscous oil whose molecular weight and

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(15) W. H. Watson, Jr., *et. al.*, *J. Polymer Sci.*, **55**, 137 (1961).

(16) Dr. Karl Klager, Aerojet-General Corp., Sacramento, Calif., private communication.

(17) L. Merriwether, *J. Org. Chem.*, **26**, 5155 (1961).

infrared spectrum showed it to be a mixture of 1,2,4- and 1,3,5-trimethylolbenzene.

Polyakova's polymer does not show the 1020-cm.$^{-1}$ *trans* absorption band, indicating lack of stereoregularity in his polymer, as would be expected from a thermal polymerization.

Chlorination of Polyacetylene.—Polyacetylene (10 g.) which had been thoroughly washed to remove catalyst residues (1.5% present during chlorination) was reacted with chlorine in carbon tetrachloride for 4 hr. at room temperatures. Chlorine was added periodically to keep the carbon tetrachloride saturated. The black polyacetylene was gradually converted to a fibrous, white solid. After filtration and washing with fresh carbon tetrachloride, the product was dried to constant weight under vacuum, yielding 27.5 g.

Anal. Calcd. for $\mathrm{+CHCl{-}CHCl+_{\mathit{n}}}$: C, 24.77; H, 2.08; Cl, 73.15. Found: C, 31.35; H, 2.68; Cl, 62.8; ash, 2.8.

Natta[1] reported a white, chlorinated product of 62–68% chlorine. Our product on standing about 6 months evolved small amounts of HCl, apparently by dehydrochlorination, as would be expected for this structure.

Results and Discussion

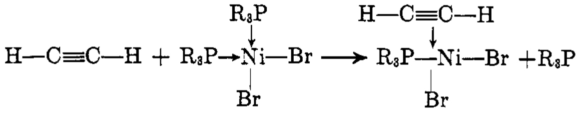
When acetylene is bubbled through an ethanol solution of $\mathrm{NiBr_2\cdot 2Ph_3P}$ at room temperature, a sequence of color changes occurs. First, the original green color fades after about 5 min. and a straw-colored solution results. After another 5-min. period, the color deepens quickly, passing through orange, red, and finally black, at which point it is seen that a finely divided, black solid is present. Little polymer is formed under these conditions, however, and autoclave polymerizations were found to give good yields of polyacetylene. Table I illustrates the effectiveness of nickel halide–tertiary phosphine complexes as catalysts for the polymerization of acetylene. Screening experiments employed the catalyst at 0.01 *M* concentration, ambient temperatures, and a mixture of nitrogen and acetylene as feed gas, as illustrated in the Experimental section.

These data indicate that the polymerization of acetylene is initiated in some way at the dative bond of the complexes in which the acceptor atom is specifically nickel, and the donor atom is specifically phosphorus. The large increase in yield on passing from 100% THF as solvent to 10% THF–90% EtOH may reflect the lower coordinative power of ethanol as compared with THF for nickel bromide.

The reaction mixture loses catalytic activity as the polymerization proceeds. Little more polymer forms after 24 hr. In fact, the filtered solutions after product isolation were always seem to have lost the original green color, and were no longer active toward fresh acetylene.

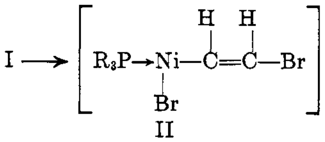
The fact that the nickel content of polyacetylene is removed completely by anhydrous HCl in chloroform while halogen is retained, may mean that nickel and halogen are present as end groups, the halogen as alkyl halide, and the nickel as labile organometallic.

The specificity of the system $\mathrm{X_2Ni{\rightarrow}PR_3}$ as a catalyst for the polymerization of acetylene suggests that the initial step in the polymerization is a displacement of one or more phosphine ligands by acetylene to form a transient π-complexed acetylene intermediate which leads to polymer by a cycle of ligand insertion and monomer complexation.



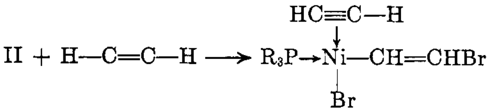
$$\mathrm{H{-}C{\equiv}C{-}H + R_3P{\rightarrow}\underset{\underset{Br}{|}}{\overset{\overset{R_3P}{\downarrow}}{Ni}}{-}Br \longrightarrow R_3P{-}\underset{\underset{Br}{|}}{\overset{\overset{H-C\equiv C-H}{\downarrow}}{Ni}}{-}Br + R_3P} \quad (1)$$

I



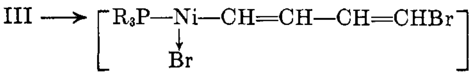
$$\mathrm{I \longrightarrow \left[R_3P{\rightarrow}\underset{\underset{Br}{|}}{Ni}{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}Br \right]} \quad (2)$$

II



$$\mathrm{II + H{-}C{=}C{-}H \longrightarrow R_3P{\rightarrow}\underset{\underset{Br}{|}}{\overset{\overset{HC\equiv C-H}{\downarrow}}{Ni}}{-}CH{=}CHBr} \quad (3)$$

III

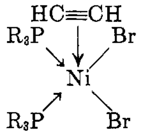


$$\mathrm{III \longrightarrow \left[R_3P{-}\underset{\underset{Br}{\downarrow}}{Ni}{-}CH{=}CH{-}CH{=}CHBr \right]} \quad (4)$$

IV

IV now has a vacant coordination site and can add fresh acetylene as in eq. 3, repeating the cycle of complexation and monomer addition as in eq. 4.

An alternative reaction path lies in direct acetylene complexation to form a pentacoordinate π-complex in which Ni has attained the Kr configuration. V could be expected to lead to polymer in the same way as I.



V

The complete removal of Ni from polyacetylene with HCl, while halogen is retained, is consistent with the above interpretation.

The mechanism of termination is more difficult to picture, but polymer insolubilization very likely plays a large role. The fate of nickel remaining in solution is unknown.

Acknowledgment.—The author wishes to thank the General Aniline and Film Corporation for permission to publish this work. He also thanks Mr. Robert Fredericks for X-ray analyses, Mr. David Lynch for infrared interpretations, Messrs. Kenneth Young, John Carberry, and Walter Haney for technical assistance, Mr. Louis Frauenfelder for elemental analyses, Drs. O. F. Hecht, M. E. Chiddix, and S. A. Glickman for helpful discussions, and many people of the laboratory who have otherwise helped in this work. Special thanks to Dr. H. S. Schultz for a critical reading of this manuscript.