The Polymerization of Acetylenes with Dicyclopentadienyl-vanadium

By Ryuichiro TSUMURA and Nobue HAGIHARA

(Received August 18, 1964)

Although a large number of organometallic complexes have been reported in which aromatic rings such as cyclopentadienyl and benzene are coordinated to the transition metals, their possible catalyses have not yet been extensively studied. It has previously been shown in our laboratory that the oxygenated product of dibenzene-chromium has a catalytic activity of the polymerization of ethylene.1) We will now report that paramagnetic dicyclopentadienylvanadium2) (I) catalytically polymerizes various acetylenes. This seems to be the first example of the polymerization of acetylenes with metallocene only.

As a typical experiment, in a 100 ml. stainless steel autoclave 0.375 g. (2.07 mmol.) of I was dissolved in 50 ml. of benzene under nitrogen. Acetylene was introduced to about 15 kg./cm^2. The reaction system was then continuously shaken and maintained under the pressure of 15～22 kg./cm^2, by means of the occasional addition of acetylene, at 80°C for 6 hr. When the reaction muds were treated with a solution of methanol and hydrochloric acid (1 : 1 by volume) under nitrogen, they gave 2.85 g. of a black solid (Found: C, 87.94; H, 7.34; Ash, 0.00%). In a similar reaction in toluene, no liquid products such as benzene and linear oligomers were found.

The black solid was thermally stable at 200°C and insoluble in all organic solvents. The infrared spectrum was essentially identical to that of the conjugated *trans*-polyacetylene obtained by Natta et al.3) and by Hatano4). The polymer was gradually oxidized when left standing in air, in a few months changing into an orange solid whose infrared spectrum showed

---

1) H. Yamazaki, M. Yamaguchi and N. Hagihara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 959 (1962); *Annual Reports of the Institute for Fibre Research*, **16**, 495 (1963).

2) E. O. Fischer and S. Vigoureux, *Chem. Ber.*, **91**, 2205 (1958).

3) G. Natta, G. Mazzanti and P. Corradini, *Atti. Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, **25**, 3 (1958).

4) M. Hatano, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 723 (1962).

TABLE I. THE POLYMERIZATION OF ALKYNES WITH I[a]

Alkyne g.	Catalyst g.	Conversion %	Product[b]		Mixture of trimers		
			Cyclic trimer g.	Oligomer g.	Ratio[c] 1, 3, 5-/ 1, 2, 4-	B. p. °C	n_D^{20}
$CH_3C\equiv CH$ 7.0	0.445	34.6	2.32	0.10	42/58	165∼70	1.5057
n-$C_3H_7C\equiv CH$ 11.04	0.464	74.8	8.02	0.25	36/64	101/3 mmHg	1.4930
n-$C_4H_9C\equiv CH$ 10.45	0.453	67.4	6.85	0.20	35/65	134/3 mmHg	1.4902
$C_6H_5C\equiv CH$ 8.60	0.385	98.8	Dimer 0.3	8.2	M. p.	Oligomer 123∼125°C,	M. w. 493[d]

a) The alkyne and catalyst I were dissolved in 30 ml. of benzene under nitrogen, and the solution was heated at 100°C in an ampule for 5 hr. (1-alkynes) or for 4 hr. (phenylacetylene).

b) The liquid products were separated by distillation, and the solid products were isolated by reprecipitation.

c) The proportion of 1, 3, 5- to 1, 2, 4-trisubstitution was determined by gas chromatographic analyses.

d) By the cryoscopic benzene method.

the presence of carbonyl and hydroxyl groups. A suspension of the black polymer in carbon tetrachloride added chlorine to give a white solid, which was then soluble in dimethyl formamide. These facts indicate that the black solid obtained may be a linear, high-molecular-weight polymer, containing quite long sequences of conjugated double bonds in the trans configuration.

1-Alkynes have been polymerized by catalyst I, too. The experimental results are summarized in Table I. The infrared spectra of the products showed that they are composed of mixtures containing 1, 3, 5- and 1, 2, 4-trialkylbenzene as the major products and a small quantity of higher oligomers. *t*-Butylacetylene was inert in the catalytic reaction; a bulky *t*-butyl radical is presumed to hinder cyclotrimerization by the catalyst.

Phenylacetylene gave an orange-yellow solid, whose infrared spectrum and molecular weight indicate that it may be a linear oligomer in the trans configuration. No cyclization to benzene derivatives was observed in this reaction. Attempts to polymerize propargyl alcohol and disubstituted acetylenes, such as 3-heptyne, 2-butyne-1, 4-diol, and tolane, were unsuccessful.

It is of great interest that the catalysis of dicyclopentadienyl-vanadium is remarkably selective, as has been mentioned above, and different from that[5] of bis(triphenylphosphine)-dicarbonyl-nickel in the catalytic polymerization of acetylenes. In relation to this problem, we have prepared some new, highly air-sensitive acetylene complexes such as π-$C_5H_5(C_2H_2)$-$V(CO)_2$. The investigation of the acetylene complexes of vanadium will be published elesewhere.

The Institute of Scientific
and Industrial Research
Osaka University
Sakai, Osaka

---

[5] L. S. Meriwether, M. F. Leto, E. C. Colthup and G. W. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962).