The Polymerization of Acetylene with Dicyclopentadienyl-titanium

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It has previously been discovered that ethylene and propylene can easily be polymerized to polymers of a high crystallinity with a catalyst of titanium trichloride, polymethylhydrosiloxane and dicyclopentadienyl-titanium (DCT).[1] It has now been discovered that DCT is a good catalyst for the polymerization of acetylene also. Although a similar finding has been reported on the catalysis of dicyclopentadienyl-vanadium (DCV),[2] it is less reactive than DCT in the polymerization of acetylene under mild conditions.

DCT was prepared by the reduction of dicyclopentadienyl-titanium dichloride with sodium amalgam (the sodium concentration was 0.1 wt. % in mercury) in toluene under an argon atmosphere.[1]

As a typical experiment, 40 ml. of a toluene solution containing 0.24—1.0 mmol. of DCT was added to a 100-ml. three-necked flask equipped with a gas inlet, a gas outlet and a thermometer, under an argon atmosphere. Acetylene was then introduced, with vigorous agitation, through the gas inlet from a gas burette. The polymerization proceeded rapidly but was stopped after 60 min. at 30°C. Black or reddish-black solid polymers were obtained; no liquid products were found. No polymers were obtained with DCV under similar conditions. The results of the experiments are shown in Table I.

In an attempt to ascertain the properties of the polyacetylene obtained, 3.5% of it was extracted by boiling it with benzene for 12 hr. under an argon atmosphere. From infrared examinations it was elucidated that it contained trans-double bonds and that carbonyl groups were formed by exposure to air for a long time. The X-ray diffraction showed a sharp peak at $d=3.8$ Å, indicating the high crystallinity of the polymer. According to the thermal differential analysis, it was gradually oxidized by air, but it was stable in inert gas up to about 300°C. Those properties were the

1) K. Shikata, K. Yokokawa, S. Nakao and K. Azuma, to be published.
2) R. Tsumura and N. Hagihara, This Bulletin, 37, 1889 (1964).

TABLE I. THE POLYMERIZATION OF ACETYLENE

No.	DCT* mmol.	[DCT]* mmol./l.	C_2H_2 mmHg	Temp. °C	Time min.	Solid product g.
1	1.0	25	760	80	60	1.04
2	1.0	25	760	30	60	0.84
3	1.0	25	760	−15	60	0.68
4	1.0	25	760	−50	60	0.45
5	1.0	25	760	−65	60	0.32
6	0.5	13	760	30	60	0.46
7	0.24	6	760	30	60	0.16
8	0.24	6	150	20	60	0.1
9	0.24	6	150	−70	60	0.1
10**	6.0	25	760	30	60	3.2
11***	1.0	25	770	27	60	0.0
12***	1.0	25	770	75	180	0.0

* The amount of DCT in the toluene solution was determined by the concentration of titanium as titanium dioxide. Forty milliliters solution was used in each experiment except No. 10.

** 240 ml. solution was used in a 300-ml. three necked flask.

*** In the experiments of No. 11 and No. 12, DCV was used in place of DCT. It was prepared in the same method as DCT, by the reduction of dicyclopentadienyl-vanadium dichloride with sodium amalgam.

same as those of the conjugated *trans*-polyacetylene obtained by Natta et al.[3] and by Hatano[4]. The polyacetylene obtained with DCT may be assumed to be similar to that obtained with DCV.[2]

In considering the catalytic behavior of metallocene, it is very interesting that acetylene polymerizes more easily with DCT than with DCV.

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3) G. Natta, G. Mazzanti and P. Corradini, *Atti. Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 25, 3 (1958); G. Natta, P. Pino and G. Mazzanti, Japanese Pat. 10597 (1957).

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