Polymer Bulletin 2, 823–827 (1980)

Polymer Bulletin

Polymerization of Acetylene Derivatives Induced by UV Irradiation via Metal Carbonyls

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SUMMARY: The polymerization of phenylacetylene induced by UV irradiation of $W(CO)_6$ in carbon tetrachloride provided in high yield a polymer, whose molecular weight reached about 80,000. The polymerization did not proceed without UV irradiation or in the absence of a halogen-donating agent such as carbon tetrachloride. On the other hand, the polymerization of 2-chloro-1-phenylacetylene was best effected by $Mo(CO)_6$, and did not require any halogen-donating agent (polymer MW 400,000). Polymerization of other acetylene derivatives was also examined.

INTRODUCTION

We have reported that phenylacetylene is polymerized by WCl_6 and $MoCl_5$ to give polymers with molecular weights up to 15,000 (MASUDA et al. 1974). Further, the structure of polymers (MASUDA et al. 1975) and the polymerization of phenylacetylene derivatives (MASUDA et al. 1979) have been investigated in detail.

In the course of our study on the catalysis of VIA metal carbonyls, $M(CO)_6$ (M = Cr, Mo, W), we found that $Mo(CO)_6$ effected the polymerization of 2-chloro-1-phenylacetylene to give a linear high polymer in high yield and that this polymerization was very much depressed in the dark. Furthermore, the polymerization of phenylacetylene by $W(CO)_6$ under UV irradiation proved to need certain halogen-donating agents as solvents or sensitizers. These interesting findings prompted us to clarify the behavior of polymerization of acetylene derivatives induced by UV irradiation of VIA metal carbonyls.

It is noted that olefin metathesis also can take place by UV irradiation of $W(CO)_6$ in carbon tetrachloride solution (KRAUSZ et al. 1975, AGAPIOU and MCNELIS 1975, KRAUSZ et al. 1976). Recently it has been reported that carbene derivatives of tungsten

0170-0839/80/0002/0823/$01.00

carbonyl catalyze the polymerization of acetylenes (KATZ, LEE 1980).

EXPERIMENTAL

Phenylacetylene was prepared by the bromination of styrene and the subsequent dehydrobromination. 2-Chloro-1-phenylacetylene was donated by Sanyo Chemical Industries Ltd. Other acetylenes were commercially obtained. Metal carbonyls were purchased from Strem Chemicals, Inc.

A 300 W high pressure mercury lamp (Eikosha Model PIH-300, Japan) was used to irradiate catalyst solutions or polymerization solutions. Both solutions were kept in the dark whenever UV irradiation was not applied. All the polymerization procedures were carried out under a dry nitrogen atmosphere. Monomer conversions were determined by gas chromatography (GC). Number-average molecular weights of polymers were measured by the osmotic pressure method using a Mechrolab 502 osmometer.

RESULTS AND DISCUSSION

Polymerization of Phenylacetylene. A solution of $W(CO)_6$ (0.10 mmol) in carbon tetrachloride (5.0 mL) was irradiated with UV light at 30°C for 1 h. To the solution was added a solution of phenylacetylene (10 mmol, 1.10 mL) and chlorobenzene (0.50 mL, as internal standard of GC) in carbon tetrachloride (3.4 mL), and the mixture was kept in the dark at 30°C for 24 h.

TABLE I

Polymerization of Phenylacetylene by VIA Metal Carbonyls[a)]

No	Catalyst	Solvent	Irradn. Time, h	Convn, %	$\bar{M}_n$
1	$W(CO)_6$	CCl_4	1	92.9	76900
2	$Mo(CO)_6$	"	1	7.9	
3	$Cr(CO)_6$	"	1	0.0	
4	$W(CO)_6$	Toluene	1	0.0	
5	"	CCl_4	0	0.0	
6	"	"	1/2	90.7	78800
7	"	"	2	96.4	76600

a) Polymerized at 30°C for 24 h after catalyst solutions were irradiated at 30°C: $[M]_0$ = 1.0 M, [Cat] = 10 mM.

The polymer formed was isolated by precipitation in methanol. Monomer conversion exceeded 90% (Table I, No 1), and the yield of isolated polymer was found to be in good agreement with the monomer conversion.

When the polymerization was carried out with $Mo(CO)_6$ or $Cr(CO)_6$ instead of $W(CO)_6$, the monomer conversions were 7.9% and 0.0%, respectively; thus the kind of metal greatly affected catalyst activity. The polymerization did not proceed at all either in toluene or without UV irradiation, which indicates that both carbon tetrachloride and UV light are essential factors. This polymerization also took place in the presence of carbon tetrachloride, carbon tetrabromide or ethyl trichloroacetate (concn. 1.0 M) as sensitizers in toluene solution.

Molecular weights of polymers reached about 80,000 (see Table I). These values are by far the highest among the molecular weights of poly(phenylacetylene) ever reported. The polymers had the form of dark red powder. The IR spectrum of the polymer was identical to that of poly(phenylacetylene) obtained with WCl_6 (MASUDA et al. 1975).

Polymerization of 2-Chloro-1-phenylacetylene. A solution of $Mo(CO)_6$ (0.30 mmol), 2-chloro-1-phenylacetylene (10 mmol, 1.22 mL) and tetralin (0.60 mL, as internal standard of GC) in toluene (8.18 mL) was irradiated at 30°C for 30 min, and then kept in the dark at 30°C for 23.5 h. Then about 85% of the feed monomer was consumed (Table II, No 1), which was quantitatively recovered as a methanol-insoluble polymer. Thus the polymerization of 2-chloro-1-phenylacetylene did not need carbon tetrachloride, indicating that an active

TABLE II

Polymerization of 2-Chloro-1-phenylacetylene by VIA Metal Carbonyls[a)]

No	Catalyst	Irradn Time, h	Convn, %	$M_n \times 10^{-4}$
1	$Mo(CO)_6$	1/2	85.9	43.2
2	$W(CO)_6$	1/2	6.7	
3	$Cr(CO)_6$	1/2	0.0	
4	$Mo(CO)_6$	0	8.2	
5	"	1/6	77.1	37.2
6	"	1	83.0	

a) Polymerized in toluene at 30°C for 24 h under UV irradiation for initial given periods: $[M]_0 = 1.0$ M, [Cat] = 30 mM.

TABLE III

Polymerization of Other Acetylene Derivatives by VIA Metal Carbonyls[a)]

No	Monomer	Catalyst	Convn, %
1	1-Hexyne	$W(CO)_6$	57.5
2	"	$Mo(CO)_6$	11.7
3	*tert*-Butylacetylene	"	96.5
4	Propargyl Chloride	$W(CO)_6$	24.4
5	"	$Mo(CO)_6$	7.0

a) Polymn. conditions: See Table I, Nos 1,2 for 1-hexyne and *tert*-butylacetylene, and Table II, Nos 1,2 for propargyl chloride.

species can be formed from $Mo(CO)_6$ and the monomer by UV irradiation.

The polymerization proceeded only slightly with $W(CO)_6$, which contrasts with the result that phenylacetylene was best polymerized by $W(CO)_6$. The polymerization did not occur with $Cr(CO)_6$. As shown in Table II, even $Mo(CO)_6$ could hardly catalyze the polymerization in the dark.

The polymer molecular weights were as high as 400,000. To our knowledge, these values are the highest among the molecular weights of polymers from disubstituted acetylenes. The polymer was in the form of yellowish white powder, and soluble in aromatic hydrocarbons and halogenated hydrocarbons.

Polymerization of Other Acetylene Derivatives. Polymerizations of 1-hexyne, *tert*-butylacetylene, propargyl chloride, 3-hexyne, 1-phenylpropyne and diphenylacetylene were tried by use of the present catalyst systems. As a consequence, 1-hexyne, *tert*-butylacetylene and propargyl chloride gave polymers (see Table III); the last monomer was polymerized in the absence of carbon tetrachloride in the same way as 2-chloro-1-phenylacetylene. The poly(1-hexyne) obtained was a reddish yellow tacky polymer, poly(*tert*-butylacetylene) a white solid (polymer MW 292,000), and poly(propargyl chloride) a black powder. Unlike 2-chloro-1-phenylacetylene, disubstituted acetylenes such as 3-hexyne, 1-phenylpropyne and diphenylacetylene were hardly polymerized under the conditions applied for the polymerization of phenylacetylene.

In conclusion, the polymerization of phenylacetylene and 2-chloro-1-phenylacetylene induced by UV irradiation of VIA metal carbonyls took place in excellent polymer yields to provide polymers having very high molecular weights.

Acknowledgments

The authors thank Sanyo Chemical Industries, Ltd. for providing 2-chloro-1-phenylacetylene. Thanks are also due to Dr. Toshiro Masuda for his assistance in measuring polymer molecular weights.

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Received June 18, 198o
Revised and accepted July 7, 198o