

Synthesis of High Polymers from Disubstituted Acetylenes using Halides of Niobium(v) and Tantalum(v) as Catalysts†

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When oct-3-yne and 1-phenylprop-1-yne are polymerised by halides of Nb^V and Ta^V white soluble polymers are obtained whose weight-average molecular weights exceed one million.

Acetylene has successfully been polymerized by Ziegler-type catalysts, and extensive studies have been carried out related to the conductivity of doped polyacetylene.¹ Disubstituted acetylenes cannot be polymerized by Ziegler-type catalysts, however, owing to steric hindrance. We have found that many disubstituted acetylenes form high-molecular-weight polymers in the presence of Mo- and W-based catalysts.² Recently Cotton *et al.* have reported on organo-Nb^{III} and -Ta^{III} complexes as catalysts for the polymerization of disubstituted acetylenes;³ these complexes are, however, air-sensitive and rather difficult to prepare. We report here a simple synthesis of high polymers from oct-3-yne and 1-phenylprop-1-yne with simple halides of Nb^V and Ta^V as catalysts.

Unless otherwise specified, the polymerizations were carried out under dry nitrogen in toluene at 80 °C, [monomer]₀ = 1.0 M, [cat] = 0.020 M, for 24 h. The weight-average molecular weights, \overline{M}_w , of the polymers were determined by the light-

scattering method, and the number-average molecular weights, \overline{M}_n , of the oligomers by vapour pressure osmometry.

Oct-3-yne afforded polymers when NbX₅ and TaX₅ (X = Cl, Br, and I) were used as catalysts (see Table 1). Some polymer molecular weights reached a few million. In many cases a cyclotrimer was formed simultaneously. A relatively high temperature of 80 °C was required to achieve high polymer yields. Hydrocarbons and halogenated hydrocarbons served as polymerization solvents. Oct-2-yne produced a mixture of linear oligomer (\overline{M}_n 3500) and cyclotrimer with NbCl₅ and only the cyclotrimer with TaCl₅. Oct-4-yne was polymerized by NbCl₅ and TaCl₅ to give a white, poorly soluble polymer.

1-Phenylprop-1-yne provided a high polymer when TaBr₅ was used as catalyst. Its molecular weight exceeded one million under the appropriate polymerization conditions (Table 1). Again some cyclotrimer was formed. On the other hand, all other halides of niobium(v) and tantalum(v) gave only a linear oligomer (\overline{M}_n ca. 4000) and/or the cyclotrimer.

The i.r., ¹H, and ¹³C n.m.r. spectral data supported the

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Table 1. Polymerization of oct-3-yne and 1-phenylprop-1-yne.^a

Monomer	Catalyst	% Yield		Polymer $\overline{M}_w/10^5$
		Polymer	Cyclo-trimer	
Oct-3-yne	NbCl ₅	100	0	2.1
Oct-3-yne	NbBr ₅	38	62	2.8
Oct-3-yne	NbI ₅	56	15	18
Oct-3-yne	TaCl ₅	82	8	8.8
Oct-3-yne	TaBr ₅	43	57	32
MeC≡CPh	TaBr ₅	57	25	9.2
MeC≡CPh ^b	TaBr ₅	54	34	17
MeC≡CPh ^c	TaBr ₅	72	14	15

^a Polymerized in toluene at 80 °C for 24 h; [monomer]₀ = 1.0 M, [cat] = 0.020 M. ^b Polymerized at 100 °C. ^c Polymerized in cyclohexane.

conjugated polyene structures, $[-C\equiv C-Cu^0-]_n$ and $[-CMe=CPh-]_n$ for poly(oct-3-yne) and poly(1-phenylprop-1-yne), respectively. These polymers are white, soluble, air-stable, electrical insulators (σ ca. 1×10^{-18} ohm⁻¹ cm⁻¹), and show no paramagnetism, in striking contrast with polyacetylene.¹ This may be due to the fact that the main chain of polymers formed from disubstituted acetylenes can assume only a twisted conformation.

The present polymerization has the following characteristics. (i) The catalysts are commercially available, and easy to handle since they are stable to air, (ii) disubstituted acetylenes provide polymers, whereas monosubstituted acetylenes selectively give cyclotrimers,⁴ and (iii) the observed molecular

weights are extremely high compared with those normally attained by acetylenic polymers.

The W-catalysed polymerization of acetylenes proceeds via metal carbenes and metallacyclobutenes in a manner similar to olefin metathesis.⁵ Further, carbene complexes of Nb and Ta give rise to olefin metathesis.⁶ Therefore, we suggest that metal carbene complexes may be formed in the present system and may effect acetylene polymerization via metallacyclobutenes. These metallacyclobutenes may mediate in the propagation.

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