# Polymerization of Alkoxyacetylenes

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Acetylene and its derivatives are known to undergo polymerization to linear polymers or cyclic oligomers depending on the polymerization conditions.[1] Alkoxyacetylene gives an interesting linear polymer which is susceptible to chemical transformations because of its unsaturated ether structure. There have been, however, only a few reports on its polymerization. Phenoxyacetylene has been polymerized thermally to a cross-linked polymer.[2] Ethoxyacetylene has been reported to give a cyclic trimer in the presence of $Ni(CO)_2(PPh_3)_3$.[3]

Since alkoxyacetylene was expected to polymerize cationically by analogy with vinyl ether, the polymerization of methoxy- and isobutoxyacetylene were attempted in the presence of Friedel-Crafts catalysts and soluble Ziegler catalysts, which were known to be effective for acetylene.

Monomers were prepared according to a known procedure.[4] Methoxyacetylene, bp 23.5°C; isobutoxyacetylene, bp 46.0—47.0°C/135 mmHg, $n_D^{20}$ 1.4022.

The cationic polymerization was carried out in either *n*-hexane or methylene chloride (20 m*l*) at −78°C for 3 hr, using 2 m*l* of isobutoxyacetylene and a 0.1 mol equivalent of a catalyst. The polymerization was then quenched by the addition of methanol, followed by evaporation; this gave a 39% yield with $TiCl_4$ in methylene chloride, a 55% yield with $BF_3$ (saturated), and a 18% yield with $AlBr_3$. Catalysts such as $BF_3 \cdot Et_2O$, $SnCl_4$ and $VCl_3$ gave yields of only a few percentage points. The polymerizations in *n*-hexane resulted in lower yields than those in methylene chloride.

Soluble complex catalysts composed of transition-metal acetylacetonate and triisobutylaluminum (1 : 1) were found to be very effective. Polymerizations were carried out in benzene (20 m*l*) at 30°C for 3 hr, using 2 m*l* of isobutoxyacetylene and a 0.1 mole quivalent of the complex catalysts. These polymerizations were stopped by the addition of methanol, and the whole contents were evaporated. The yields were calculated using the correction of the catalyst residue, the following yields being found for the given acetylacetonate: $Fe^{3+}$ 92, $Cr^{3+}$ 91, $Co^{3+}$ 89, $VO^{2+}$ 81, $Ni^{2+}$ 59, $Co^{2+}$ 46, $Cu^{2+}$ 42, $V^{3+}$ 25, $TiO^{2+}$ 16, $Zr^{4+}$ 0, $Mn^{3+}$ 0, $Zn^{2+}$ 0%. It is interesting to note that $Cr^{3+}$, $Fe^{3+}$ and $Cu^{2+}$ had scarcely been at all effective in the polymerization of acetylene.[5]

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[1] E. M. Smolin and D. S. Hoffenberg "Encyclopedia of Polymer Science and Technology," Vol. I, ed. by H. F. Mark, N. G. Gaylord and N. M. Bikales, Interscience Publishers, New York, N. Y. (1964), p. 46.

[2] T. L. Jacobs and W. P. Tuttle, Jr., *J. Am. Chem. Soc.*, **71**, 1313 (1949).

[3] L. S. Meriwether, E. C. Colthup, G. W. Kennerly and R. N. Reusch, *J. Org. Chem.*, **26**, 5155 (1961).

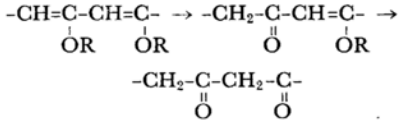
[4] J. F. Arens, "Advances in Organic Chemistry," Vol. 2, ed. by R. A. Raphael, E. C. Taylor and H. Wynberg, Interscience Publishers, New York, N. Y. (1963), p. 117.

[5] S. Kambara, M. Hatano and T. Hosoe, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **65**, 720 (1962).

The cationic polymers were viscous or tacky semisolids, in color ranging from a light brown to a reddish brown, and in molecular weight ranging around 500—600. The absence of IR absorption bands of trisubstituted benzene and NMR resonance due to aromatic hydrogen suggests a negligible formation of cyclic trimers, if any.*2

The polymers which were obtained with the Ziegler catalysts were partly soluble in methanol. The soluble part was a reddish-brown, tacky solid and resembled the cationic polymer. The insoluble part was a brown-to-black powder. Both the parts contained an inorganic ingredient originating from the catalyst, and purification was found to be difficult. For example, when a 0.1 mol equivalent of $Fe(acac)_3$-$Al(i\text{-}Bu)_3$ (1 : 1) to the monomer was used, the soluble part of the poly(isobutoxyacetylene) was found to contain 8.6% ash, and the insoluble part, 10.6%. The Al/Fe atomic ratio in the latter was found to be 0.31. Upon treatment with aqueous 2 N HCl, the polymer was almost free from ash, which amounted to only 0.28% in the soluble part and 0.51% in the insoluble part. Unfortunately, however, the treatment was accompanied by a chemical modification of the polymer, as will be mentioned below.

A crude poly(methoxyacetylene) showed in its infrared apectrum a broad band of a polyconjugated double bond around 1560 $cm^{-1}$ (s), an ether linkage at around 1080(s), and an olefinic C–H bond at 820 $cm^{-1}$(m). On treatment with 2 N HCl, all these bands diminished in intensity, and new bands appeared around 1715(s), 1660(s) and 1600(s) $cm^{-1}$; these bands are considered to be due to various kinds of carbonyls. Poly(isobutoxyacetylene) showed essentially the same spectral change and weight loss of 20% upon treatment with 2 N HCl, followed by heat-treatment at 90°C. As a volatile product of the treamtent, isobutanol was identified by gas chromatography. Hence, the spectral change may be interpreted by the following reaction scheme:



$$-CH=\underset{OR}{C}-CH=\underset{OR}{C}- \rightarrow -CH_2-\underset{O}{\overset{}{C}}-CH=\underset{OR}{C}- \rightarrow -CH_2-\underset{O}{C}-CH_2-\underset{O}{C}-$$

In fact, the methanol-insoluble part of poly(methoxyacetylene) after the treatment with 2 N HCl showed the following analytical data, which correspond to those where 3/5 of the enol-ether structure was converted into ketone.

Found: C, 60.61; H, 5.40%. Calcd for $[(C_3H_4O)_2(C_2H_2O)_3]_n$: C, 60.50; H, 5.88%.

The halogenation of the polymers was attempted in chloroform at room temperature, 75—93% of the theoretical value of chlorine and 56—68% of that of bromine were introduced, a process accompanied by a slight evolution of hydrogen halide. The halogenated polymers were soluble in acetone and benzene. The molecular weight of the chlorinated poly(methoxyacetylene) were found by vapor-pressure osmometry to be 560 and 800 for the soluble and insoluble parts respectively, and the chlorine contents, 41.74 and 49.79% respectively.

The hydrogenation of the crude poly(isobutoxyacetylene) was attempted using Pd or Pt on carbon as a catalyst or with tri-*n*-butylboron,6) but no hydrogenation was observed. Diels-Alder reactions with maleic anhydride or maleimide in refluxing toluene gave negative results.

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*2 When ethoxyacetylene was treated with $TiCl_4$ in benzene at 40°C for 3 hr, there was obtained a polymer in a 51% yield; from this a cyclic trimer (13%, mp 35—36°C) was isolated by alumina-column chromatography.

6) F. L. Ramp, E. J. Dewitt and L. E. Trapasso, *J. Org. Chem.*, **27**, 4368 (1962).