

Poly(1-chloro-oct-1-yne): a New, High-molecular-weight Polyacetylene synthesized with Molybdenum Catalysts

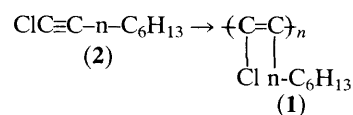
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1-Chloro-oct-1-yne polymerizes in the presence of Mo catalysts [*e.g.*, MoCl₅, MoCl₅-Buⁿ₄Sn, Mo(CO)₆-CCl₄-*hν*] to give a new, high-molecular-weight (\bar{M}_w up to 1×10^6), white, soluble, air-stable, electrically insulating polyacetylene, which is the first example of a polymer from a chlorine-containing aliphatic disubstituted acetylene.

Acetylene can be polymerized by Ziegler catalysts such as Ti(OBuⁿ)₄-Et₃Al.¹ In contrast, acetylenes with bulky substituent(s) provide polymers in the presence of group 6 (Mo, W)² and 5 (Nb, Ta)³ transition metal catalysts. There have, however, been rather few examples of the formation of polymers from heteroatom-containing disubstituted acetylenes: *e.g.*, 1-chloro-2-phenylacetylene,⁴ 1-(trimethylsilyl)-prop-1-yne.⁵ 1-Chloroalk-1-yne have often been used to compare structure and reactivity with those of the corresponding alk-1-yne and 1-chloroalk-1-ene.^{6,7} Here we report the synthesis of a new, high-molecular-weight polymer (1) from

the monomer 1-chloro-oct-1-yne (2), and describe its polymer properties.



1-Chloro-oct-1-yne was prepared from oct-1-yne according to the literature method.⁸ Catalysts and cocatalysts were employed as purchased. The polymerization was carried out

Table 1. Polymerization of 1-chloro-oct-1-yne.^a

Catalyst	Monomer conversion/%	Yield/%	Polymer (1) ^b $\bar{M}_w/10^3$	$[\eta]^\epsilon/\text{dL g}^{-1}$
MoCl ₅	100	78	220	0.95
MoCl ₅ -Bu ⁿ Li	100	86	820	3.78
MoCl ₅ -Et ₃ Al	100	55	780	2.89
MoCl ₅ -Bu ⁿ ₄ Sn	100	92	870	2.80
MoCl ₅ -Ph ₃ Bi	100	93	520	2.16
Mo(CO) ₆ -CCl ₄ -hν ^d	90	85	1200	6.96

^a Polymerized in toluene at 30 °C for 24 h; [monomer]₀ = 0.50 M, [MoCl₅] = [cocat] = 0.020 M. ^b Methanol-insoluble parts. ^c Intrinsic viscosities measured in toluene at 30 °C. ^d Polymerized in CCl₄; [Mo(CO)₆] = 0.010 M.

under dry nitrogen. Weight-average molecular weights, \bar{M}_w , of the polymers were determined by gel permeation chromatography on the basis of a polystyrene calibration.

Only Mo catalysts yielded methanol-insoluble polymers from 1-chloro-oct-1-yne among Ziegler catalysts [Ti(OBuⁿ)₄-Et₃Al and Fe(acac)₃-Et₃Al (Hacac = MeCOCH₂COMe)] and various group 5 and 6 transition metal catalysts^{2,3} exploited by us. Even MoCl₅ alone formed in ca. 80% yield a polymer having \bar{M}_w of ca. 2×10^5 (Table 1). However, 1:1 mixtures of MoCl₅ with suitable organometallic cocatalysts achieved still higher yields and/or \bar{M}_w of polymer; for instance, when Buⁿ₄Sn was used as cocatalyst, a polymer with \bar{M}_w up to 9×10^5 formed in over 90% yield. The high molecular weights of the polymers are endorsed by their intrinsic viscosities $[\eta]$ (Table 1).

The effects of solvent and temperature were examined by using MoCl₅-Buⁿ₄Sn(1:1) as catalyst under the conditions shown in Table 1. Polymerization proceeded not only in toluene but also in many other hydrocarbon and halogenated hydrocarbon solvents; e.g., polymer yield/% ($\bar{M}_w/10^3$): 92 (560) in cyclohexane, 93 (580) in hexane, 92 (430) in CCl₄, 91 (320) in (CH₂Cl)₂. The polymer yield was not dependent on polymerization temperature, while \bar{M}_w decreased slightly with increasing temperature; polymer yield/% ($\bar{M}_w/10^3$): 86 (830) at 0 °C, 92 (870) at 30 °C (Table 1), 88 (410) at 60 °C, and 89 (560) at 80 °C.

A catalyst obtained by u.v. irradiation of a CCl₄ solution of Mo(CO)₆ [Mo(CO)₆-CCl₄-hν]⁴ provided in high yield a polymer whose \bar{M}_w exceeded 1×10^6 (Table 1). Polymerization with this catalyst occurred at 30 °C or above, and \bar{M}_w decreased with increasing temperature; polymer yield/% ($\bar{M}_w/10^3$): 0 (-) at 0 °C, 85 (1200) at 30 °C (Table 1), 86 (1000) at 60 °C, and 94 (670) at 80 °C. The corresponding W(CO)₆-CCl₄-hν also catalyses olefin metathesis,⁹ and the present polymerization of acetylenes by group 5 and 6 transition metal catalysts is inferred to proceed *via* metal carbenes as in olefin metathesis.^{2,10}

The polymer formed is the first example of a polymer from a chlorine-containing aliphatic disubstituted acetylene. Satisfactory analytical data were obtained. The spectral data (for the polymer sample obtained with MoCl₅-Buⁿ₄Sn in Table 1) are as follows: i.r. (KBr) 2950s, 2850s, 1660—1600w, 1460m, 1380w, 1100w, 920w, 800w, and 740w cm⁻¹; ¹³C n.m.r. δ (CDCl₃) 14.0(C-8), 22.6(C-7), 27.8(C-3), 29.7(C-4), 31.6(C-5, C-6), 129.0(C-1), and 136.8(C-2). These data support the polymer having alternating double bonds along the main chain, *i.e.* as shown in structure (1).

Poly(1-chloro-oct-1-yne) is a white solid which shows a weak maximum (ϵ 720 mol dm⁻³ cm⁻¹) at 280 nm and no

absorption above 320 nm in the u.v.-visible spectrum in hexane solution. This indicates that the main chain assumes a twisted conformation owing to the steric effect of substituents. The exponent, *a* in the equation, $[\eta] = K\bar{M}_w^a$, was around unity (in Table 1), being larger than the values (*a* = 0.5—0.8) for most vinyl polymers; this implies the polymer is more rigid than vinyl polymers, and therefore supports a twisted, sterically less hindered conformation. According to X-ray diffraction, this polymer was amorphous. It completely dissolved in hydrocarbons (toluene, hexane *etc.*) and halogenated hydrocarbons (CCl₄, CHCl₃, *etc.*). Solution casting afforded a tough polymer film.

The softening point of this polymer was 170—200 °C. When the polymer was heat-treated in air at 120 °C for 20 h, its \bar{M}_w hardly decreased (8.7×10^5 to 6.7×10^5). The weight loss of the polymer began in air at ca. 310 °C in thermogravimetric analysis (heating rate: 10 °C/min). These results show that this polymer is much more stable than polyacetylene. The electrical conductivity was 4×10^{-18} S cm⁻¹, in a typical insulator range.

Synthesis and characterization of a series of poly(1-chloroalk-1-yne)s, polyacetylenes of a new category, are now under way.

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