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Preparation of Polycyclooctyne by Ring-Opening Polymerization Employing d^0 Tungsten and Molybdenum Alkylidyne Complexes

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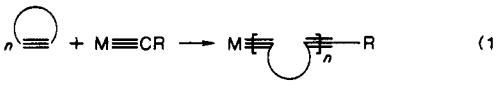
ABSTRACT: Polycyclooctyne ("polyoctynamer") can be prepared by adding cyclooctyne (up to 500 equiv) to $W_2(O\text{-}t\text{-}Bu)_6$ in toluene (preferably) or dichloromethane. Polyoctynamer has a T_m = 62 (±4) °C, a T_g = −65 (±8) °C, and a decomposition temperature of 390 °C. Samples could be hydrogenated to give polyethylene, which had a polydispersity between 4 and 7. Mass spectra of cyclooctyne oligomers (5 equiv), prepared by quenching living oligomers with benzoic acid and methanol, were consistent with the presence of macrocycles rather than linear molecules. Analogous oligomers and polymers can be prepared by using $Mo(CR)(O\text{-}t\text{-}Bu)_3$ species as catalysts and quenching with phenylacetylene. Oligomers prepared by quenching after short reaction times consist of linear species, $(HC)[C(CH_2)_6C]_n(CPr)$, as well as macrocyclic species, but if the reaction is quenched after 15 min of reaction time, only macrocycles are observed in a distribution predicted by the Jacobson–Stockmayer relationship. These results suggest that secondary metathesis of triple bonds in the polymer is a significant complication in the molybdenum system as well as the tungsten system, although it is much slower in the molybdenum system. Other results corroborate these findings, among them the fact that $Mo(CR)(O\text{-}t\text{-}Bu)_3$ complexes *will* react with internal acetylenes (several equivalents in minutes) if R is not *tert*-butyl. Attempts to prepare polyoctynamer by adding cyclooctyne to $W(CR)(DIPP)_3$ (DIPP = 2,6-diisopropylphenoxide) yielded only relatively stable tungstacyclobutadiene complexes. Metathesis of 2,8-dodecadiyne by a $W(CR)(O\text{-}t\text{-}Bu)_3$ complex also yields polyoctynamer (plus 2-butyne), whose T_m is virtually identical with that prepared from cyclooctyne. Complexes of the type $(t\text{-}BuO)_3W{\equiv}C(CH_2)_xC{\equiv}W(O\text{-}t\text{-}Bu)_3$ were prepared for x = 0, 2, 4, 5, and 6.

Introduction

Ring-opening polymerization of cyclic olefins by classical olefin metathesis catalysts is well-known.[1] In the past few years, well-characterized catalysts have been discovered that allow living polymers of certain cyclic olefins to be prepared.[2] Since acetylene metathesis catalysts of the type $M(CR')(OR)_3$ are known,[3] and since their activity can be controlled through choice of M (Mo or W) and OR (O-*t*-Bu, $OCMe_2(CF_3)$, O-2,6-C_6H_3-*i*-Pr_2, etc.), it should be possible to ring-open polymerize a cyclic acetylene under the right circumstances (eq 1) to give a living polymer, i.e., one in



(1)

which the terminal M≡C bond does not react readily with a triple bond in the chain (either intramolecularly, to give cyclic oligomers, or intermolecularly). Cyclooctyne is an interesting possibility for a reaction of this type since it has a significant amount of ring strain[4] and therefore should be more reactive than the triple bonds in the polymer. In this paper we evaluate the ring-opening metathesis polymerization of cyclooctyne using d^0 alkylidyne complexes as catalysts. A preliminary communication on this subject has appeared.[5]

Results and Discussion

Ring-Opening Metathesis of Cyclooctyne by $W_2(O\text{-}t\text{-}Bu)_6$. $W_2(O\text{-}t\text{-}Bu)_6$ is an interesting potential ring-opening catalyst for cyclooctyne for several reasons. First, $W_2(O\text{-}t\text{-}Bu)_6$ is known to react readily with disubstituted acetylenes to give alkylidyne complexes of the type $W(CR)(O\text{-}t\text{-}Bu)_3$.[6] Therefore, the first product of the reaction between cyclooctyne and $W_2(O\text{-}t\text{-}Bu)_6$ should be $(t\text{-}BuO)_3W{\equiv}C(CH_2)_6C{\equiv}W(O\text{-}t\text{-}Bu)_3$. Subsequent reaction of $(t\text{-}BuO)_3W{\equiv}C(CH_2)_6C{\equiv}W(O\text{-}t\text{-}Bu)_3$ with cyclooctyne at each W≡C bond should give a polymer of the type $(t\text{-}BuO)_3W[C(CH_2)_6C]_nW(O\text{-}t\text{-}Bu)_3$. This approach eliminates the need of preparing $W(CR)(O\text{-}t\text{-}Bu)_3$ compounds separately. A second reason is that $W_2(O\text{-}t\text{-}Bu)_6$ can be prepared in relatively large quantities from readily available starting materials. Finally, Freudenberger[7] has shown that treatment of $W(CR)(O\text{-}t\text{-}Bu)_3$ complexes with 2 equiv of carboxylic acids initially protonates the alkylidyne carbon atom to give an alkylidene ligand, which then rearranges to an olefin that can be displaced by PMe_3 or upon treatment with methanol. Therefore, the polymer should be removed cleanly from the metal center:

$$(t\text{-}BuO)_3W[C(CH_2)_6C]_nW(O\text{-}t\text{-}Bu)_3 \xrightarrow[\text{methanol}]{2RCO_2H} [H_2C{=}CH(CH_2)_5C]_2[C(CH_2)_6C]_{n-2} \quad (2)$$

Addition of n equiv (n = 10–500) of cyclooctyne to a toluene solution of $W_2(O\text{-}t\text{-}Bu)_6$ at 25 °C gives a gelatinous polymer in a few minutes. The reaction was quenched by adding benzoic acid followed by methanol. Polymerization in pentane gives a polymer with similar properties but with a more fibrous structure. Polymers prepared in either manner, where $n \gg 50$, are insoluble in toluene (80 °C, 4 days), methylene chloride (40 °C, 1 day), 1,2,4-trichlorobenzene (140 °C, 2 days), *o*-dichlorobenzene (140 °C, 2 days), and tetrahydrofuran (25 °C, 2 weeks). "Polyoctynamer" swells and expands when exposed to aromatic solvents and methylene chloride. Exposure of swelled samples to nonpolar and especially oxygenated solvents (ethers, alcohols) removes the aromatic solvent

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Table I
IR (cm^{-1}) and NMR (δ, ppm) Data for Cyclooctyne, Polyoctynamer, and 1,9-Cyclohexadecadiyne

compd	IR	^1H NMR	^{13}C NMR
cyclooctyne	2260/2206, CCl_4[d]	H(β) 1.98	C(α) 94.5[b]
	2290/2210, neat	H(γ) 1.62	C(β) 35.2
		H(δ) 1.46	C(γ) 30.4
			C(δ) 21.3
polyoctynamer	no absorption at 2200; strong absorption at 725	H(β) 2.10	C(α) 80.1[c]
		H(γ) 1.42	C(β) 29.1
		H(δ) 1.30	C(γ) 28.4
			C(δ) 18.7
1,9-cyclohexadecadiyne	no absorption at 2200	H(β) 2.16	C(α) 80.6[a]
		H(γ) 1.52	C(β) 29.1
		H(δ) 1.38	C(γ) 27.7
			C(δ) 18.5

[a] In C_6D_6. [b] In toluene-d_8. [c] In $CDCl_3$. [d] Meier, H.; Petersen, H.; Kolshorn, H. *Chem. Ber.* **1980**, *113*, 2398.

and gives an insoluble white powder. The polymer also can be prepared in dichloromethane.

An oligomeric sample suitable for ^1H and ^{13}C NMR analysis was prepared by adding 20 equiv of cyclooctyne to $W_2(O\text{-}t\text{-}Bu)_6$ in methylene chloride. The solvent was removed *in vacuo* after 5–10 min, and the sample was taken up in deuteriochloroform. A ^{13}C NMR spectrum exhibits a resonance at 80.4 ppm that is shifted significantly from that for cyclooctyne at 94.5 ppm (Table I), similar to that in 1,9-cyclohexadecadiyne. The range of chemical shifts of acetylenic carbon atoms in linear acetylenes is 75–90 ppm, while the range of chemical shifts for olefinic carbon atoms is 100–145 ppm. On this basis, we contend that a ring opening has occurred, rather than 1,2-polymerization to give a polyene. Other chemical shifts in polyoctynamer are similar to those in 1,9-cyclohexadecadiyne (Table I). Therefore, it is not possible to decide on the basis of these NMR data alone whether the polymer has a linear or a macrocyclic structure.

Polymer samples were characterized by differential scanning calorimetry (DSC) and differential mechanical thermal analysis (DMTA). DSC thermograms (Figure 1) showed a polymer melting temperature (T_m) of 62 (±4) °C, glass transition temperature (T_g) of −65 (±8) °C, and a decomposition temperature of 390 °C. DMTA yielded values for T_m and T_g that were identical with those obtained by DSC. The low T_m might be expected on the basis of the trend in T_m for polyoctenamer (82 °C)[8] and polyethylene (138 °C).[9] Polyoctynamer readily breaks apart above its T_m.

The IR spectrum of polyoctynamer lacks the $\nu_{C\equiv C}$ absorptions at 2260 and 2206 cm^{-1} found in cyclooctyne, as would be expected for a triple bond in an ordinary linear acetylene, and a new strong absorption is found at 725 cm^{-1}. These data again do not distinguish between a linear and a cyclic structure.

Polyoctynamer obtained with $n \gg 50$ was too insoluble at 25 °C for GPC analysis. Attempts to solubilize the polymer by functionalization of the acetylenic unit met with limited success. Titration of polyoctynamer (n = 100) in toluene with bromine to an end point where a brown color persisted showed that approximately 1 equiv of bromine was absorbed. The resulting insoluble white polymer did not swell and qualitatively appeared to be at least as insoluble as polyoctynamer itself.

Selective hydrogenation of polyoctynamer to polyoctenamer was also attempted. Selective hydrogenation with $[Rh(NBD)(PMe_2Ph)_3][PF_6]$[10] was not successful, as polyoctynamer was not soluble enough in the appropriate solvent (THF, 2-ethoxyethanol, or acetone). $AlH(i\text{-}Bu)_2$ does not add to the triple bond in polyoctynamer (n = 100) in toluene since hydrolysis gave polyoctynamer back again unchanged.

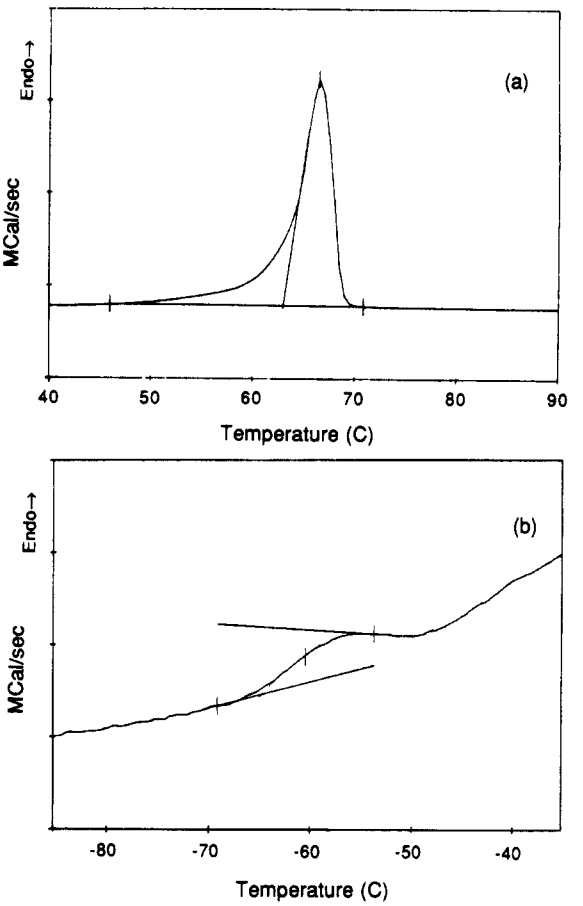


Figure 1. Differential scanning calorimetry of polyoctynamer (n = 250): (a) scan rate 10° min^{-1}; (b) 20° min^{-1}.

Table II
Gel Permeation Chromatographic Analysis of Fully Hydrogenated Polyoctynamer[a]

cyclooctyne, equiv	M_w	M_n	M_w/M_n	M_n (theory)
250	26 000	4300	6.1	27 000
350	33 000	7500	4.4	37 900
500	60 000	8600	7.0	54 100

[a] Polyoctynamer samples were hydrogenated at 60 psig of H_2 and 40 °C for 16 h in toluene with $Rh(PPh_3)_3Cl$ as the catalyst. The resulting polyethylene was analyzed at 145 °C in 1,2,4-trichlorobenzene on a Waters 150C instrument equipped with three Styragel columns. A single relatively symmetric peak was observed in each case. The columns were calibrated with polystyrene standards in the usual way. The usual conversion factor of 4.1 was employed in order to obtain the molecular weight.

Hydrogen of polyoctynamer (n = 100) with $Rh(PPh_3)_3Cl$ (40 °C, 60 psig H_2, 16 h, toluene) yielded polyethylene, according to ^1H NMR, DSC (T_m = 135 °C), and IR studies. The results of high-temperature GPC analysis of the polyethylene prepared in this manner are shown in Table II. M_n increases in proportion to the number of equivalents of cyclooctyne added, a result that suggests that this polymerization reaction is living to some extent. However, the polydispersities are much too large for the polymer to have resulted from a well-behaved ring-opening polymerization reaction.[2] Possible sources of the high polydispersity are hydrogenolysis, relatively poor initiation relative

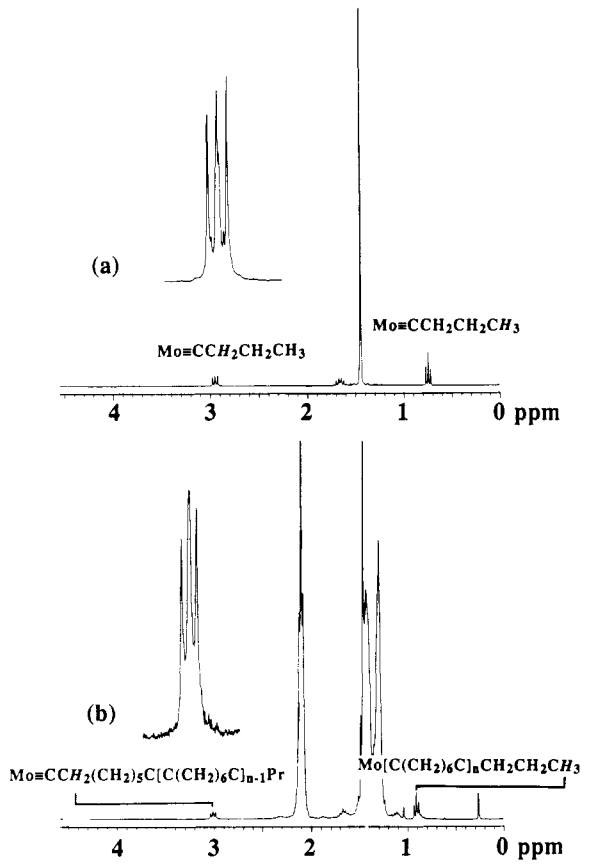


Figure 2. 300-MHz ^{1}H NMR spectra in C_6D_6 (a) of Mo(CPr)(O-*t*-Bu)$_3$ and (b) after the addition of 15 equiv of cyclooctyne to Mo(CPr)(O-*t*-Bu)$_3$.

to propagation, back-biting into the polymer chain to give cyclics, or degradation of the living polymer (loss of activity) over time before quenching.

Mass spectroscopy was employed to determine if cyclics were being formed. A sample prepared by addition of 5 equiv of cyclooctyne to W_2(O-*t*-Bu)$_6$ followed by benzoic acid and methanol was examined by GC/MS. *tert*-Butyl alcohol and 1,9-cyclohexadecadiyne were observed but *not* cyclooctyne. Electron impact mass spectra showed that the sample also contained parent ions with masses consistent with macrocycles of the formulation $[C(CH_2)_6C]_n$ (n = 2–7) rather than linear species with m/e values two units higher. Therefore, we conclude that the majority of the polymer has a macrocyclic, not a linear, structure. This result is not especially surprising since W(CR)(O-*t*-Bu)$_3$ complexes are known to be excellent catalysts for the metathesis of ordinary internal acetylenes,[3] and therefore should not discriminate well between cyclic and acyclic triple bonds. Use of W(CR)(O-*t*-Bu)$_3$ complexes rather than W_2(O-*t*-Bu)$_6$ would not solve the problem, the only difference being the possibility of monometallic species being involved in the catalytic cycle.

Preparation of Polyoctynamer Employing Mo(CPr)(O-*t*-Bu)$_3$. Mo(CR)(O-*t*-Bu)$_3$ complexes are much less active acetylene metathesis catalysts than W(CR)(O-*t*-Bu)$_3$ complexes; e.g., Mo(C-*t*-Bu)(O-*t*-Bu)$_3$ does not react readily with 3-heptyne, although it will react readily with 1-pentyne (eq 3).[3d] Mo(CPr)(O-*t*-Bu)$_3$ will very slowly

$$\text{Mo(C-}t\text{-Bu)(O-}t\text{-Bu)}_3 + \text{HC}{\equiv}\text{CPr} \rightarrow \text{Mo(CPr)(O-}t\text{-Bu)}_3 + t\text{-BuC}{\equiv}\text{CH} \quad (3)$$

catalyze the metathesis of 3-heptyne over several hours at 25 °C in benzene or toluene. The most characteristic features in the ^{1}H NMR spectrum of Mo(CPr)(O-*t*-Bu)$_3$ in C_6D_6 (Figure 2a) are signals for the Mo≡CCH_2CH$_2$CH$_3$ protons at 2.95 ppm and the Mo≡CCH$_2$CH$_2$CH_3 protons at 0.74 ppm. Upon addition of 15 equiv of cyclooctyne, these signals are replaced by analogous resonances that one might assign to Mo([C(CH$_2$)$_6$C]$_n$CPr)(O-*t*-Bu)$_3$ (Figure 2b); the Mo≡CCH_2R signal can be seen clearly at 3.02 ppm and the signal for the methyl group in the propyl cap at 0.92 ppm. Unfortunately, n cannot be determined on the basis of the NMR spectrum. Addition of a 20-fold excess of phenylacetylene to Mo(CPr)(O-*t*-Bu)$_3$ cleaves the metal from the polymer (eq 4) within 15 min in greater than 95%

$$(t\text{-BuO})_3\text{Mo}[\text{C}(\text{CH}_2)_6\text{C}]_n(\text{CPr}) + \text{PhC}{\equiv}\text{CH} \rightarrow (t\text{-BuO})_3\text{Mo}{\equiv}\text{CPh} + (\text{HC})[\text{C}(\text{CH}_2)_6\text{C}]_n(\text{CPr}) \quad (4)$$

yield (by ^{1}H NMR). Addition of pentane precipitated a white powder whose ^{13}C NMR spectrum is shown in Figure 3. The carbon signals for this product are identical with those found for the material prepared by adding 20 equiv of cyclooctyne to W_2(O-*t*-Bu)$_6$. Since resonances for carbon atoms in the capping groups are absent, we can propose that the product prepared with Mo(CPr)(O-*t*-Bu)$_3$ also consists largely of cyclic oligomers analogous to those generated in the reaction involving W_2(O-*t*-Bu)$_6$, *not* linear (HC)[C(CH$_2$)$_6$C]$_n$(CPr).

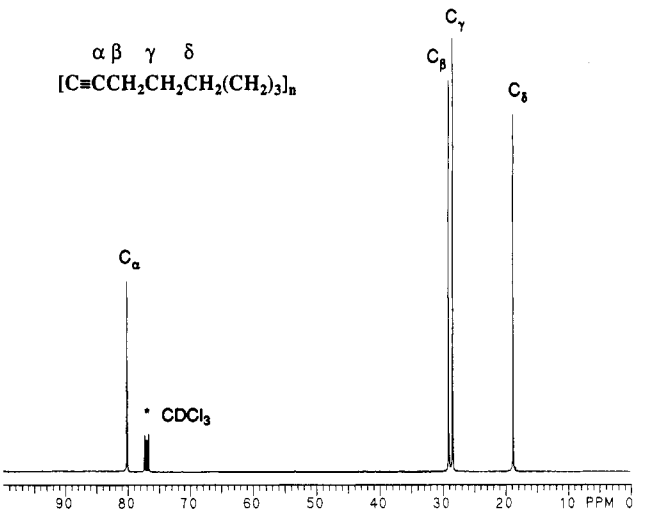


Figure 3. 100.6-MHz ^{13}C NMR spectrum in $CDCl_3$ of polyoctynamer prepared by adding 15 equiv of cyclooctyne to Mo(CPr)(O-*t*-Bu)$_3$ followed by quenching with phenylacetylene.

The molecular structure of cyclooctyne oligomers prepared by employing Mo(CPr)(O-*t*-Bu)$_3$ as the catalyst was investigated by EI mass spectroscopy. Mo(CPr)(O-*t*-Bu)$_3$ was treated with 7.5 equiv of cyclooctyne, and the reaction was quenched after 2 min with excess phenyl acetylene. The EI mass spectrum of the product (lower spectrum in Figure 4) showed molecular ion peaks for the expected linear species, (HC)[C(CH$_2$)$_6$C]$_n$(CPr) (m/e 500, 608, 716, etc.) *and* cyclic species (m/e 324, 432, etc.), with peaks for the linear species dominating. No difference was observed in spectra of products formed in reactions that were allowed to stand for up to 24 h before being quenched. In a sample quenched after 15 min, only peaks for the cyclic species were found (upper spectrum in Figure 4). These results suggest that Mo([C(CH$_2$)$_6$C]$_n$CPr)(O-*t*-Bu)$_3$ intermediates *do* react readily with the triple bonds in the growing polymer to give cyclic oligomers and new Mo([C(CH$_2$)$_6$C]$_m$CPr)(O-*t*-Bu)$_3$ species ($m < n$). This is a disappointing result and one that is contrary to our initial proposal[5] that the molybdenum catalyst system constitutes a well-behaved (irreversible) living polymerization. It does appear to be the case, however, that metathesis of the triple bonds in the growing polymer *is* much slower for molybdenum than for tungsten, since a similar sample

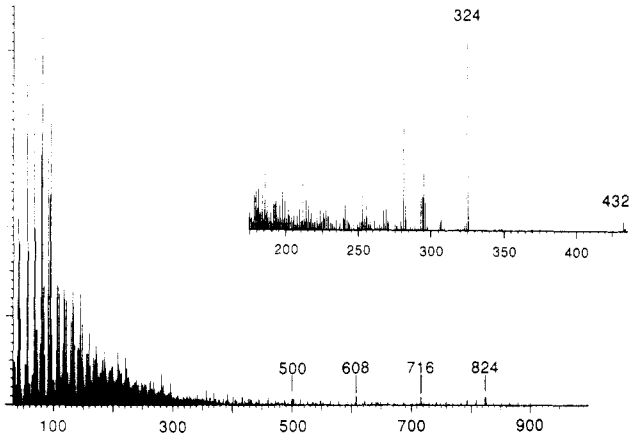


Figure 4. Electron impact mass spectroscopy of polyoctynamer prepared by adding 7.5 equiv of cyclooctyne to Mo(CPr)(O-*t*-Bu)$_3$ followed by quenching with phenylacetylene. The molecular ion peaks for the linear species are labeled in the lower spectrum (sample quenched after 2 min) and those for the macrocyclic species in the upper spectrum (sample quenched after 15 min).

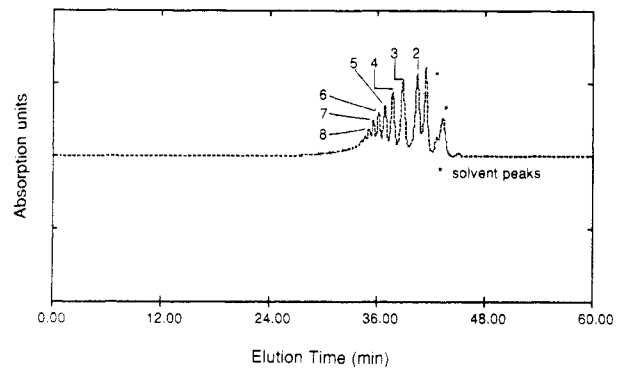


Figure 5. GPC analysis of polyoctynamer prepared by adding 8 equiv of cyclooctyne to Mo(CPr)(O-*t*-Bu)$_3$ followed by quenching with phenylacetylene. The time between peak maxima is ~7 s. Numbers correspond to x in [C(CH$_2$)$_6$C]$_x$, as judged by comparison with the GPC results for 1,9-cyclohexadecadiyne (x = 2) under identical conditions.

prepared with W(CEt)(O-*t*-Bu)$_3$ followed by quenching with phenylacetylene less than 1 min after addition of cyclooctyne consisted solely of cyclic oligomers. We can also conclude that the cyclics observed in the W$_2$(O-*t*-Bu)$_6$ system above arise because of the inherent reactivity of W≡C bonds toward ordinary internal olefins, rather than some unique feature of the W$_2$(O-*t*-Bu)$_6$ system itself.

GPC analysis of sample prepared by adding 7.5 equiv of cyclooctyne to Mo(CPr)(O-*t*-Bu)$_3$ followed by quenching with phenylacetylene clearly shows a distribution of cyclic oligomers that is consistent with that predicted by the Jacobson–Stockmayer relationship[11] (Figure 5). Comparison of double log plots of [M]$_n$ vs n for polyoctynamer and polyoctenamer[12] confirm Jacobson–Stockmayer behavior (a slope of −3.1 and −2.6, respectively, Figure 6). This result reinforces the conclusion that back-biting is occurring to generate the equilibrium mixture of cyclic oligomers.

Other evidence for cyclic oligomers has been obtained by ^{1}H NMR studies. If 1–20 equiv of cyclooctyne are added to Mo(CPr)(O-*t*-Bu)$_3$, all of the cyclooctyne is consumed, but not all Mo(CPr)(O-*t*-Bu)$_3$ is converted into Mo([C(CH$_2$)$_6$C]$_n$(CPr))(O-*t*-Bu)$_3$, and the relative amounts of Mo(CPr)(O-*t*-Bu)$_3$ and Mo([C(CH$_2$)$_6$C]$_n$(CPr))(O-*t*-Bu)$_3$ vary according to the amount of cyclooctyne added. The results of two separate sets of experiments are shown together in Table III and Figure 7. The data fit nicely on a curve described by the equation $y = 1/(2n + 1)$, where

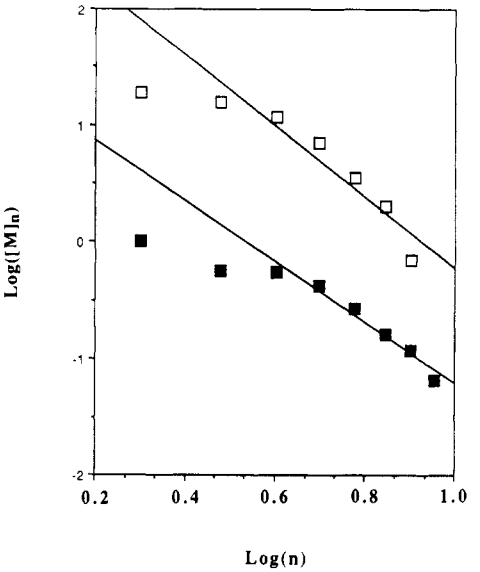


Figure 6. Jacobson–Stockmayer plots of polyoctenamer (solid squares) and polyoctynamer (open squares).

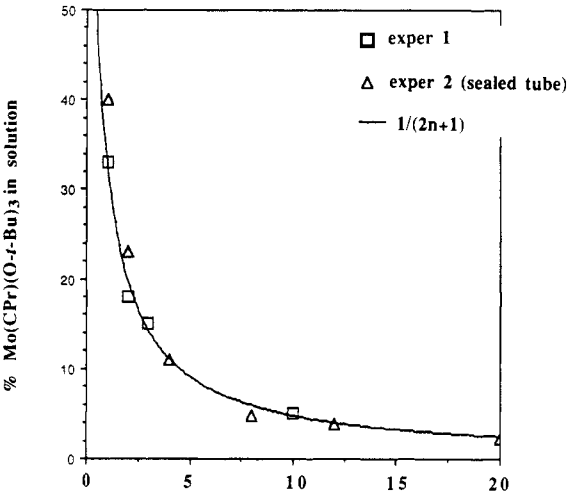


Figure 7. Plot of the equilibrium percentage of Mo(CPr)(O-*t*-Bu)$_3$ versus equivalents of cyclooctyne added.

Table III
Equilibrium Concentration of Mo(CPr)(O-*t*-Bu)$_3$ and Mo([C(CH$_2$)$_6$C]$_n$CPr)(O-*t*-Bu)$_3$

cyclooctyne, equiv	% Mo(CPr)-(O-*t*-Bu)$_3$	% Mo([C(CH$_2$)$_6$C]$_n$-CPr)(O-*t*-Bu)$_3$
1	40 (33[b])	60 (67[b])
2	23 (18[b])	77 (82[b])
3	15[b]	85[b]
4	11	89
8	4.8	95
10	5.0	95
12	3.9	96
20	2.3	98

[a] Cyclooctyne in 0.75 mL of C$_6$D$_6$ was added rapidly to a stirred solution of 10 mg of Mo(CPr)(O-*t*-Bu)$_3$ and *p*-dichlorobenzene (internal standard) in 1.5 mL of C$_6$D$_6$. The ratio of Mo(CPr)(O-*t*-Bu)$_3$ to Mo([C(CH$_2$)$_6$C]$_n$CPr)(O-*t*-Bu)$_3$ was determined by integration after 24 h. In several analogous experiments, the equilibrium values did not change after heating the samples at 100 °C for 10 min. [b] These values were obtained in a separate set of analogous experiments.

y is the percentage of Mo(CPr)(O-*t*-Bu)$_3$ left in solution and n is the initial ratio of cyclooctyne to Mo(CPr)(O-*t*-

Bu)$_3$. We also know that when a sample of Mo([C-(CH_2)$_6$C]$_n$(CPr))(O-*t*-Bu)$_3$ prepared from 15 equiv of cyclooctyne is mixed with an equal amount of Mo(CPr)(O-*t*-Bu)$_3$, the amount of Mo(CPr)(O-*t*-Bu)$_3$ slowly decreases, and an equilibrium mixture consisting of ~8% Mo(CPr)(O-*t*-Bu)$_3$ and 92% Mo([C(CH_2)$_6$C]$_m$(CPr))(O-*t*-Bu)$_3$ is established after several hours. Incorporation of Mo(CPr)(O-*t*-Bu)$_3$ into the polymer proves that the triple bonds in the growing polymer are being attacked.

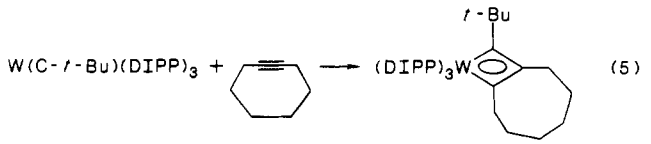
Finally, reactions between Mo(CPr)(O-*t*-Bu)$_3$ and 1,9-cyclohexadecadiyne were investigated. A ^{1}H NMR spectrum of "Mo([C(CH_2)$_6$C]$_n$(CPr))(O-*t*-Bu)$_3$" (average initial n = 15) at 120 °C showed no sign of cyclooctyne (≤2% estimated; ~2% of the sample decomposed) or 1,9-cyclohexadecadiyne. However, when 0.63 equiv of 1,9-cyclohexadecadiyne was added to Mo(CPr)(O-*t*-Bu)$_3$, an equilibrium mixture consisting of 33% Mo(CPr(O-*t*-Bu)$_3$ to 97% Mo([C(CH_2)$_6$C]$_m$(CPr))(O-*t*-Bu)$_3$ was established in ~1 h. This result suggests that Mo(CPr)(O-*t*-Bu)$_3$ reacts with the triple bonds in 1,9-cyclohexadecadiyne and presumably other cyclic oligomers formed during ring-opening polymerization.

Since previous studies suggested that Mo(CR)(O-*t*-Bu)$_3$ reacts slowly (if R is small) or virtually not at all (if R = *t*-Bu) with 3-hexyne or 3-heptyne, we reinvestigated that reacitivity more closely. Mo(C-*t*-Bu)(O-*t*-Bu)$_3$ will react with 4 equiv of 2-butyne at room temperature to afford Mo(CMe)(O-*t*-Bu)$_3$ and *t*-BuC≡CMe in 60% yield after 72 h and at 70 °C to afford Mo(CMe)(O-*t*-Bu)$_3$ in 60% yield in 1 h. However, Mo(C-*t*-Bu)(O-*t*-Bu)$_3$ will not react with 3-hexyne even at elevated temperatures. In contrast, Mo(CPr)(O-*t*-Bu)$_3$ will react with 4 equiv of 2-butyne at room temperature to afford Mo(CMe)(O-*t*-Bu)$_3$ in 95% yield in <30 min and with 4 equiv of 3-hexyne at 40 °C to afford Mo(CMe)(O-*t*-Bu)$_3$ in 95% yield in 1 h. The large increase in reactivity of Mo(CPr)(O-*t*-Bu)$_3$ relative to Mo(C-*t*-Bu)(O-*t*-Bu)$_3$ must be ascribed to the significantly smaller steric bulk of a propyl group relative to a *tert*-butyl group in an already crowded coordination environment.

Competition studies support the above conclusions. 1,5-Heptadiyne reacts with Mo(CPr)(O-*t*-Bu)$_3$ to give Mo[C(CH_2)$_2$C≡CMe](O-*t*-Bu)$_3$ after 30 min, while after 2 h a 60/40 mixture of (*t*-BuO)$_3$Mo≡C(CH_2)$_2$C≡Mo(O-*t*-Bu)$_3$ and Mo[C(CH_2)$_2$C≡CCH_3](O-*t*-Bu)$_3$ is isolated upon removal of the solvent in vacuo. A pure sample of (*t*-BuO)$_3$Mo≡C(CH_2)$_2$C≡Mo(O-*t*-Bu)$_3$ can be obtained by adding 2,6-octadiyne to Mo(CPr)(O-*t*-Bu)$_3$ and heating the mixture for 2 h at 40 °C, followed by removing solvent in vacuo. The H_β resonance at δ 3.71 ppm and the C_α resonance at δ 281.4 ppm for (*t*-BuO)$_3$Mo≡C(CH_2)$_2$C≡Mo(O-*t*-Bu)$_3$ are analogous to those observed for (*t*-BuO)$_3$W≡C(CH_2)$_2$C≡W(O-*t*-Bu)$_3$ (see later).

Reactions between Trisphenoxide Complexes and Cyclooctyne. When W(C-*t*-Bu)(DIPP)$_3$ (DIPP = 2,6-diisopropylphenoxide) is treated with an internal acetylene, a metallacyclobutadiene complex forms that only slowly loses an acetylene to reform an alkylidyne complex.[3b] We wanted to explore the possibility of preparing an analogous metallacycle with cyclooctyne. Such a species might be a catalyst for ring-opening polymerization in a reaction in which opening of the metallacyclobutadiene ring is rate limiting.

Upon addition of excess of cyclooctyne to W(C-*t*-Bu)(DIPP)$_3$, some polyoctynamer is formed. If the polymer is filtered off and the solution concentrated in vacuo, dark red crystals can be isolated in 53% yield. On the basis of its NMR spectrum (and elemental analysis), the red crystalline compound is the metallacycle, W[C(*t*-Bu)C(CH_2)$_6$C](DIPP)$_3$ (eq 5). The resonance for the methylene



(5)

protons adjacent to C_α is found at 4.07 ppm as a broad triplet, and the resonances for the methylene protons adjacent to C_β are found at 3.48 ppm. The C_α resonances are found at 244.6 and 244.0 ppm and the C_β resonance at 129.8 ppm. Unfortunately, a mixture of cyclooctyne (4 equiv) and W[C(*t*-Bu)C(CH_2)$_6$C](DIPP)$_3$ in C_6D_6 remained unchanged in 2 h at 25 °C, according to its ^{1}H NMR spectrum. Therefore, W[C(*t*-Bu)C(CH_2)$_6$C](DIPP)$_3$ must be a thermodynamic product, and a minor impurity must be responsible for the ring opening of the excess cyclooctyne in the initial reaction. Heating the solution of W[C(*t*-Bu)C(CH_2)$_6$C](DIPP)$_3$ and cyclooctyne to 40 °C for 1 h leads to the formation of the *aromatic* trimer of cyclooctyne [C((CH_2)$_6$)C]$_3$ in 20% yield based on tungsten, in addition to an unidentified tungsten complex in ~50% yield. No cyclooctyne oligomers were observed. These results suggest that this approach to ring opening of cyclooctyne probably will not be successful.

Preparation of Polyoctynamer from Acyclic Diynes. Since W(CEt)(O-*t*-Bu)$_3$ reacts so readily with acyclic diynes, and since living cyclooctyne ring opening now does not appear to be possible with tungsten or molybdenum alkylidyne complexes that contain alkoxide ligands, it should be possible to prepare polyoctynamer (as a mixture of cyclic oligomers) by a condensation reaction in which 2-butyne is generated (eq 6). Refluxing a toluene solution

$$n\text{MeC}{\equiv}\text{C}(\text{CH}_2)_6\text{C}{\equiv}\text{CMe} \rightarrow \text{MeC}[\text{C}(\text{CH}_2)_6\text{C}]_n\text{CMe} + (n-1)\text{MeC}{\equiv}\text{CMe} \quad (6)$$

containing excess 2,10-dodecadiyne and W(CEt)(O-*t*-Bu)$_3$ yields an off-white insoluble powder that swells when exposed to aromatic solvents and has the same T_m as polyoctynamer prepared from cyclooctyne. We have no reason to believe that it is not polyoctynamer. Condensation polymerization probably is the preferred method of preparing polyoctynamer, given the fact that cyclooctyne is somewhat unstable and not convenient to prepare and store in large quantities.

The above result raises the possibility that other polyalkynamers might be prepared by condensation polymerization. Preliminary experiments have shown that polymers can be made from diynes in which the alkyne carbon atoms are separated by 2, 5, 6, and 7 methylene groups, but they too are relatively insoluble. For this reason, and because we are more interested in living polymerization systems, we have not pursued this approach.

Synthesis of Linked Tungsten Alkylidynes. We mentioned in the first section that the first product of the reaction between cyclooctyne and W$_2$(O-*t*-Bu)$_6$ should be (*t*-BuO)$_3$W≡C(CH_2)$_6$C≡W(O-*t*-Bu)$_3$ and in the section above that (*t*-BuO)$_3$Mo≡C(CH_2)$_2$C≡Mo(O-*t*-Bu)$_3$ can be isolated from the reaction between 2,6-octadiyne and Mo(C-*t*-Bu)(O-*t*-Bu)$_3$. Therefore, we decided to attempt to isolate (*t*-BuO)$_3$W≡C(CH_2)$_6$C≡W(O-*t*-Bu)$_3$ also and to prepare as many analogous species as possible in order to complete the series of compounds of the type (*t*-BuO)$_3$W≡C(CH_2)$_x$C≡W(O-*t*-Bu)$_3$, where x = 0–6.

Addition of 1 equiv of cyclooctyne to a ^{1}H NMR sample of W$_2$(O-*t*-Bu)$_6$ yields a spectrum that suggests that ~25% (*t*-BuO)$_3$W≡C(CH_2)$_6$C≡W(O-*t*-Bu)$_3$ forms initially; after several hours, the remaining W$_2$(O-*t*-Bu)$_6$ reacts to give (*t*-BuO)$_3$W≡C(CH_2)$_6$C≡W(O-*t*-Bu)$_3$ in high yield.[13] (*t*-

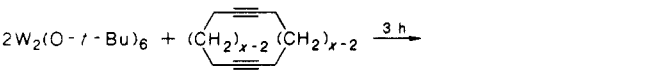
Table IV
NMR (δ, ppm) and Analytical Data for $(t\text{-BuO})_3W{\equiv}C(CH_2)_xC{\equiv}W(O\text{-}t\text{-Bu})_3$ (x = 0, 2, 4, 5, 6)

			analysis			
x	^{1}H NMR[a]	^{13}C NMR[a]	element	calcd	found	yield, %
6	H(β) 3.96	C(α) 261.69	C	42.03	41.82	50
	H(γ) 1.70	C(β) 47.25	H	7.27	7.55	
	H(δ) 1.33	C(γ) 32.98				
	O-t-Bu 1.49	C(δ) 29.52				
5	H(β) 3.98	C(α) 261.56	C	41.35	41.59	59
	H(γ) 1.72	C(β) 47.09	H	7.16	7.21	
	H(δ) 1.42	C(γ) 32.64				
	O-t-Bu 1.48	C(δ) 29.31				
4	H(β) 4.03	C(α) 261.39	C	40.83	41.21	38
	H(γ) 1.74	C(β) 47.32	H	6.62	7.13	
	O-t-Bu 1.47	C(δ) 33.03				
2	H(β) 4.45	C(α) 259.54	C	39.36	38.90	89
	O-t-Bu 1.48	C(δ) 49.92	H	6.37	6.85	
0	O-t-Bu 1.57	C(α) 278.58[b]	C	37.62	37.73	94
			H	6.55	6.67	

[a] In C_6D_6. [b] In pyridine-d_5. See ref 6b.

$BuO)_3W{\equiv}C(CH_2)_6C{\equiv}W(O\text{-}t\text{-Bu})_3$ was isolated and fully characterized (Table III). Addition of excess $W_2(O\text{-}t\text{-Bu})_6$ to polyoctynamer (n = 100) in toluene over several hours solubilizes the polyoctynamer and also eventually gives $(t\text{-BuO})_3W{\equiv}C(CH_2)_6C{\equiv}W(O\text{-}t\text{-Bu})_3$ in good yield. $(t\text{-BuO})_3W{\equiv}C(CH_2)_6C{\equiv}W(O\text{-}t\text{-Bu})_3$ is perfectly stable toward formation of cyclooctyne and $W_2(O\text{-}t\text{-Bu})_6$, as we would expect on the basis of the ring strain in cyclooctyne and the general stability of compounds of the type W(CR)(O-t-Bu)$_3$ toward formation of a W≡W bond when R is not H.[14] $(t\text{-BuO})_3W{\equiv}C(CH_2)_6C{\equiv}W(O\text{-}t\text{-Bu})_3$ also can be prepared by the reaction shown in eq 7.

Compounds with the formulation $(t\text{-BuO})_3W{\equiv}C(CH_2)_xC{\equiv}W(O\text{-}t\text{-Bu})_3$ (x = 0, 2, 4, 5, 6; Table IV) can all be prepared by the methods shown in eq 7–10 (for eq 10 see ref 6a) (solvent = toluene at 25 °C unless otherwise noted).



$$2W_2(O\text{-}t\text{-Bu})_6 + (CH_2)_{x-2}(CH_2)_{x-2} \xrightarrow{3\ h} 2(t\text{-BuO})_3W{\equiv}C(CH_2)_xC{\equiv}W(O\text{-}t\text{-Bu})_3 \quad (7)$$

x = 5, 6

$$W_2(O\text{-}t\text{-Bu})_6 + MeC{\equiv}C(CH_2)_4C{\equiv}CMe \xrightarrow[-MeC{\equiv}CMe]{2\ h} (t\text{-BuO})_3W{\equiv}C(CH_2)_4C{\equiv}W(O\text{-}t\text{-Bu})_3 \quad (8)$$

$$W_2(O\text{-}t\text{-Bu})_6 + MeC{\equiv}C(CH_2)_2C{\equiv}CMe \xrightarrow[-MeC{\equiv}CMe]{1\ h} (t\text{-BuO})_3W{\equiv}C(CH_2)_2C{\equiv}W(O\text{-}t\text{-Bu})_3 \quad (9)$$

$$W_2(O\text{-}t\text{-Bu})_6 + EtC{\equiv}C{-}C{\equiv}CEt \xrightarrow[-EtC{\equiv}CEt]{1\ h} (t\text{-BuO})_3W{\equiv}C{-}C{\equiv}W(O\text{-}t\text{-Bu})_3 \quad (10)$$

Attempts to prepare $(t\text{-BuO})_3W{\equiv}C(CH_2)_4C{\equiv}W(O\text{-}t\text{-Bu})_3$ by adding 1,7-cyclododecadiyne to $W_2(O\text{-}t\text{-Bu})_6$ failed. A green solution formed, and ^{1}H NMR analysis of the red residue obtained by removing the solvent in vacuo showed that it was composed of ~90% $W_2(O\text{-}t\text{-Bu})_6$ and less than 5% of the desired product. Increasing the reaction temperature or time did not increase the yield. Attempts to prepare $(t\text{-BuO})_3W{\equiv}C(CH_2)_3C{\equiv}W(O\text{-}t\text{-Bu})_3$ from 2,7-nonadiyne and W(CEt)(O-t-Bu)$_3$ resulted in the formation of a green solution that contained ~40% W(CEt)(O-t-Bu)$_3$ by ^{1}H NMR but little or none of the desired organometallic product. We have no explanation for the difference in the course of the reaction to prepare $(t\text{-BuO})_3W{\equiv}C(CH_2)_3C{\equiv}W(O\text{-}t\text{-Bu})_3$. We can only suggest that for x = 3 and 4 the second triple bond in the cyclic diyne coordinates to the metal center and thereby slows down productive metathesis. When solvents are removed in vacuo, productive metathesis must occur when x = 4 but only unproductive metathesis when x = 3.

With the exception of $(t\text{-BuO})_3W{\equiv}CC{\equiv}W(O\text{-}t\text{-Bu})_3$ (brown-red microcrystals), all $(t\text{-BuO})_3W{\equiv}C(CH_2)_xC{\equiv}W(O\text{-}t\text{-Bu})_3$ complexes were isolated by recrystallization from pentane at −40 °C as off-white needles. The relative solubility increases with x. ^{1}H and ^{13}C NMR are unexceptional (Table IV), the downfield shift of H_β with decreasing x presumably resulting from proximity of the second tungsten atom.

Alternative routes to $(t\text{-BuO})_3W{\equiv}C(CH_2)_xC{\equiv}W(O\text{-}t\text{-Bu})_3$ (x = 1 or 3) were sought in order to complete the series. Freudenberger synthesized several tungsten alkylidyne complexes by treating $W_2(O\text{-}t\text{-Bu})_6$ with nitriles.[15] Therefore, synthesis of $(t\text{-BuO})_3W{\equiv}CCH_2C{\equiv}W(O\text{-}t\text{-Bu})_3$ was attempted by adding malonitrile to $W_2(O\text{-}t\text{-Bu})_6$. Removal of the solvent in vacuo afforded only starting material and a complex whose ^{1}H NMR spectrum suggested that it may be an adduct, i.e., $W_2(O\text{-}t\text{-Bu})_6(N{\equiv}CCH_2C{\equiv}N)$. Likewise, the reaction between $W_2(O\text{-}t\text{-Bu})_6$ and $NCCH_xCN$ (x = 1–6) afforded only starting material and apparent adducts.

Conclusion

We conclude that living ring-opening polymerization of cyclooctyne is *not* possible even with the metathesis catalyst that has the lowest activity for metathesis of ordinary internal acetylenes (Mo(CR)(O-t-Bu)$_3$). The trade-off is that "polyoctynamer" can be prepared by a condensation polymerization. Since cyclooctyne is not reformed in the equilibrium mixture of cyclic oligomers, certain cyclic oligomers might be accessible by condensation methods under nonequilibrium conditions.[16]

Experimental Section

General Procedures. Cyclooctyne,[17] 1,9-cyclohexadecadiyne,[18] 1,5-heptadiyne,[19] $W_2(O\text{-}t\text{-Bu})_6$, W(CEt)(O-t-Bu)$_3$,[3c] and Mo(C-t-Bu)$(CH_2C\text{-}t\text{-Bu})_3$,[3d] were all prepared by published methods. Other alkynes were purchased commercially.

All manipulations were performed under dinitrogen in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride was dried over CaH_2 distilled under nitrogen and purged with nitrogen prior to use. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. 1,2,4-Trichlorobenzene and related chlorinated aromatics were dried over P_2O_5 and distilled under nitrogen. All acetylenes and NMR solvents were passed through activated alumina prior to use.

NMR data are listed in ppm relative to the proton resonances in C_6D_5H (7.15 ppm). NMR spectra were acquired at 250 or 300 MHz (^1H) and 67.9 or 100.6 MHz (^{13}C). Unless otherwise specified, spectra were obtained at room temperature in C_6D_6. Elemental analyses were performed by Schwarzkopf Microanalytical, Inc.

Hydrogenated polyoctynamer was analyzed at 145 °C in 1,2,4-trichlorobenzene on a Waters 150C instrument equipped with three Styragel columns. All other GPC analyses were done at room temperature in toluene on a Waters 150C or in methylene chloride on an instrument assembled from components (five Shodex columns and refractive index and variable-wavelength detectors). All columns were calibrated with polystyrene standards. DSC analyses were performed on a Perkin-Elmer instrument under a nitrogen atmosphere.

Preparations. 1. Polyoctynamer. A toluene solution (10 mL) of cyclooctyne (77.4 μL, 0.162 mmol) was added to a rapidly stirred solution of $W_2(O\text{-}t\text{-}Bu)_6$ (10 mg, 0.0124 mmol) in toluene (1 mL). After 15 min, benzoic acid (16 mg, 0.124 mmol) was added, and the solution was stirred for an additional 30 min. Removal of the solvent in vacuo left a pale-yellow solid in virtually quantitative yield.

Alternatively, a toluene solution (20 mL) of cyclooctyne (335 μL, 2.7 mmol) was added to a rapidly stirred solution of Mo(CPr)(O-*t*-Bu)$_3$ (10 mg, 0.027 mmol) in toluene (2 mL). After 15 min, phenylacetylene (29 μL, 0.28 mmol) was added, and the solution was stirred at room temperature for an additional 15 min. The solution was added to excess methanol (50 mL) and stood at room temperature for 1 h. An off-white polymer was obtained virtually quantitatively by decanting the solvent and was dried in vacuo.

When $n \leq 50$ an additional purification step was added, since the polymer was somewhat soluble in methylene chloride. The crude polymer was dissolved in a minimal amount of methylene chloride (10–15 mL), and the solution was filtered through Celite. An off-white precipitate was obtained by concentrating the filtrate in vacuo. Yields varied from ~40% (for $n = 20$) to ~95% (for $n = 50$).

2. Polyoctynamer for DMTA Analysis. A toluene solution (20 mL) of cyclooctyne (733 μL, 5.88 mmol) was added to a rapidly stirred solution of $W_2(O\text{-}t\text{-}Bu)_6$ (9.5 mg, 0.0118 mmol) in toluene (3 mL). After 15 min, excess pivalic acid was added (10 μL, 0.12 mmol). The well-stirred solution was poured into a 100 × 15 mm culture dish and left standing overnight under a nitrogen atmosphere. After 24 h, a light-brown film was obtained. It was dried in vacuo for 2 h and used for subsequent analysis.

3. Polyoctynamer for ^{13}C NMR Analysis. A toluene solution (1 mL) of cyclooctyne (67.4 μL, 0.54 mmol) was added to a rapidly stirred solution of Mo(CPr)(O-*t*-Bu)$_3$ (10 mg, 0.027 mmol) in toluene (1 mL). After 10 min, phenylacetylene (29 μL, mmol) was added. After an additional 5 min the solution was added to methanol (25 mL). A precipitate formed. After 30 min, the solvent was removed in vacuo, the residue was dissolved in a minimal amount of methylene chloride, and the solution was filtered through Celite. The filtrate was concentrated in vacuo to give an off-white powder (40 mg, 67%) that was used for analysis.

GC/MS and MS Analysis of 7.5 equiv of Cyclooctyne and Mo(CPr)(O-*t*-Bu)$_3$. A toluene solution (7 mL) of cyclooctyne (117.8 μL, 0.945 mmol) was added to a rapidly stirred solution of Mo(CPr)(O-*t*-Bu)$_3$ (50 mg, 0.135 mmol) in toluene (3 mL). The solution was then split into three parts. The oligomers were cleaved from the metal by adding phenylacetylene (29 μL, 0.284 mmol) to each of the three parts after 1 min, 15 min, and 24 h, respectively. In each case, the solvent was removed in vacuo, and the residue was dissolved in methylene chloride (1–2 mL) and added to methanol (25 mL). After 15 min the solvent was removed in vacuo. The residue was dissolved in minimal amount of methylene chloride (1–2 mL) and filtered through Celite. Removal of the solvent in vacuo left an off-white residue that was analyzed without further purification (^1H NMR confirmed 95% purity).

GC/MS analysis identified a high boiling compound which had a molecular ion peak corresponding to the formula $C_{16}H_{24}$. Comparison to an authentic sample confirmed that it was 1,9-cyclohexadecadiyne.

(*t*-BuO)$_3$W≡C(CH$_2$)$_6$C≡W(O-*t*-Bu)$_3$. Cyclooctyne (0.868 mmol, 108 μL) was added to a toluene (17 mL) solution of $W_2(O\text{-}t\text{-}Bu)_6$ (0.868 mmol, 0.70 g). The solution was stirred for 3 h at room temperature, eventually attaining a light-amber color. Toluene was removed in vacuo. Recrystallization of the residue from pentane at −30 °C gave white needles (0.39 g, 49%): ^1H NMR δ 3.96 (m, 2, J_{HH} = 8 Hz, WCC*H*$_2$CH$_2$CH$_2$), 1.70 (m, 2, WCCH$_2$C*H*$_2$CH$_2$) 1.49 (s, 27, OCMe$_3$), 1.33 (m, 2, WCCH$_2$CH$_2$C*H*$_2$); ^{13}C NMR δ 261.7 (s, W*C*CH$_2$CH$_2$CH$_2$), 79.7 (s, O*C*Me$_3$), 47.2 (t, $^2J_{CW}$ = 23 Hz, J_{CH} = 126 Hz, WC*H*$_2$CH$_2$CH$_2$), 33.0 (t, J_{CH} = 125 Hz, WCCH$_2$*C*H$_2$CH$_2$), 32.7 (q, J_{CH} = 126 Hz, OC*Me*$_3$), 29.5 (t, J_{CH} = 124 Hz, WCCH$_2$CH$_2$*C*H$_2$). See Table IV for analyses.

(*t*-BuO)$_3$W≡C(CH$_2$)$_5$C≡W(O-*t*-Bu)$_3$. 1,8-Cyclotetradecadiyne (0.62 mmol, 117 mg) in pentane (1 mL) was added to a pentane (10 mL) solution of $W_2(O\text{-}t\text{-}Bu)_6$ (1.24 mmol, 1.0 g). The solution was stirred at room temperature for 3 h, eventually attaining a light-amber color. Pentane was removed in vacuo. Recrystallization of the residue from pentane at −30 °C gave white needles (663 mg, 59%): ^1H NMR δ 3.98 (m, 2, J_{HH} = 8 Hz, WCC*H*$_2$CH$_2$CH$_2$), 1.72 (m, 2, WCCH$_2$C*H*$_2$CH$_2$), 1.50 (s, 27, OCMe$_3$), 1.35 (m, 1, WCCH$_2$CH$_2$C*H*$_2$); ^{13}C NMR δ 261.6 (s, W*C*CH$_2$CH$_2$CH$_2$), 79.7 (s, O*C*Me$_3$), 47.1 (t, J_{CW} = 23.5 Hz, J_{CH} = 126 Hz, WC*H*$_2$CH$_2$CH$_2$), 32.7 (q, J_{CH} = 125 Hz, OC*Me*$_3$), 32.6 (t, J_{CH} = 126 Hz, WCCH$_2$*C*H$_2$CH$_2$), 29.3 (t, J_{CH} = 123 Hz, WCCH$_2$CH$_2$*C*H$_2$). See Table IV for analyses.

(*t*-BuO)$_3$W≡C(CH$_2$)$_4$C≡W(O-*t*-Bu)$_3$. 2,8-Decadiyne (0.564 mmol, 89 μL) was added to a toluene (15 mL) solution of W(CEt)(O-*t*-Bu)$_3$ (1.13 mmol, 0.50 g). The addition resulted in a red solution that turned green within 5 min. Solvent was removed in vacuo. Recrystallization of the residue several times from pentane gave white needles (118 mg, 38%): ^1H NMR δ 4.03 (m, 2, J_{HH} = 7.3 Hz, WCC*H*$_2$CH$_2$), 1.74 (m, 2, WCCH$_2$C*H*$_2$), 1.47 (s, 27, OCMe$_3$); ^{13}C NMR δ 261.4 (s, W*C*CH$_2$CH$_2$), 79.7 (s, O*C*Me$_3$), 47.3 (t, J_{CW} = 22.7 Hz, J_{CH} = 125 Hz, WC*C*H$_2$CH$_2$), 33.0 (t, J_{CH} = 128 Hz, WCCH$_2$*C*H$_2$), 32.8 (q, J_{CH} = 126 Hz, OC*Me*$_3$). See Table IV for analyses.

(*t*-BuO)$_3$W≡C(CH$_2$)$_2$C≡W(O-*t*-Bu)$_3$. 2,6-Octadiyne (0.816 mmol, 87 mg) was added to a toluene (15 mL) solution of W(CEt)(O-*t*-Bu)$_3$ (1.63 mmol, 725 mg). After 5 min, the solvent was removed in vacuo. Recrystallization of the residue from pentane at −30 °C gave white needles (620 mg, 89%): ^1H NMR δ 4.45 (s, 2, WCC*H*$_2$), 1.48 (s, 27, OCMe$_3$); ^{13}C NMR δ 259.5 (s, W*C*CH$_2$), 79.8 (s, O*C*Me$_3$), 49.9 (t, J_{CH} = 131 Hz, WC*C*H$_2$), 32.7 (q, J_CH = 125.6 Hz, OC*Me*$_3$). See Table IV for analyses.

Observation of Mo(CMe)(O-*t*-Bu)$_3$. 2-Butyne (0.21 mmol, 13 μL) was added to a deuterated benzene (1 mL) solution of Mo(C-*t*-Bu)(O-*t*-Bu)$_3$ (0.052 mmol, 20 mg). The solution was transferred to a NMR tube, and the tube was sealed under a static vacuum. After heating to 60 °C for 2–3 h the resonances attributable to Mo(CMe)(O-*t*-Bu)$_3$ appeared in ~40% yield: ^1H NMR δ 2.58 (s, 3, Mo≡C*Me*), 1.42 (s, 27, OCMe$_3$).

(*t*-BuO)$_3$Mo≡C(CH$_2$)$_2$C≡Mo(O-*t*-Bu)$_3$. 1,5-Hexadiyne (0.585 mmol, 57 μL) was added to an ether (5 mL) solution of Mo(C-*t*-Bu)(O-*t*-Bu)$_3$ (0.195 mmol, 75 mg) and stirred at room temperature for 2 h. Solvent was removed in vacuo to give a brown residue that was 90% pure by ^1H NMR. Recrystallization from pentane at −30 °C gave low yields of the pure compound as a white powder: ^1H NMR δ 3.71 (s, 2, MoCC*H*$_2$), 1.45 (s, 27, OCMe$_3$); ^{13}C NMR δ 281.4 (s, Mo*C*CH$_2$), 79.0 (s, O*C*Me$_3$), 48.7 (t, J_{CH} = 133 Hz, MoC*C*H$_2$), 32.8 (q, J_{CH} = 124 Hz, OC*Me*$_3$).

W[C(*t*-Bu)C(CH$_2$)$_6$C][O-2,6-C$_6$H$_3$-*i*-Pr$_2$]$_3$. Cyclooctyne (0.51 mmol, 48 μL) was added to a pentane (5 mL) solution of W(C-*t*-Bu)[O-2,6-C$_6$H$_3$-*i*-Pr$_2$]$_3$ (0.25 mmol, 200 mg), and the solution was stirred for 10 minutes. The red solution was filtered through Celite to remove polymer. Removal of the solvent in vacuo left a red microcrystalline solid that could be recrystallized from pentane at −30 °C (120 mg, 53%): ^1H NMR δ 7.10, 6.90, 6.76 (m, 9, H$_o$, H$_m$, and H$_p$), 4.07 (t, 2, J_{HH} = 6 Hz, C$_\alpha$C*H*$_2$CH$_2$CH$_2$), 3.84 (sept, 2, J_{HH} = 7 Hz, C*H*Me$_2$), 3.48 (t, 2, J_{HH} = 6 Hz, C$_\beta$CH$_2$C*H*$_2$CH$_2$), 3.32 (br m, 2, C*H*Me$_2$), 2.95 (br m, 2, C*H*Me$_2$), 1.46 (s, 9, C$_\alpha$C*Me*$_3$), 1.3–0.6 (m, C$_\alpha$CH$_2$(C*H*$_2$)$_4$CH$_2$C$_\beta$ and CH*Me*); ^{13}C NMR δ 244.6, 244.0 (s, WC$_\alpha$), 160.4, 159.4 (s, C$_{ipso}$), 137.6, 137.3 (s, C$_o$), 129.8 (s, C$_\beta$), 123.7, 123.0, 122.6, 120.4 (d, J_CH = 146, 151, 153, 157 Hz, C$_m$ and C$_p$), 42.0 (s, C$_\alpha$CMe$_3$), 37.7 (t, J_{CH} = 130 Hz, C$_\alpha$CH$_2$), 33.2 (t, J_{CH} = 125 Hz, C$_\beta$CH$_2$), 32.3 (q, J_{CH} = 126 Hz, C$_\alpha$C*Me*$_3$), 30.7, 26.7, 26.8, 24.6 (t, J_{CH} = 125, 128, 127, 126 Hz, C$_\alpha$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C$_\beta$), 27.9, 26.9 (d, J_CH = 123, 128 Hz, CHMe$_2$), 24.2, 23.5 (q, J_{CH} = 128, 125 Hz, CH*Me*$_2$).

Anal. Calcd for $WC_{49}H_{72}O_3$: C, 65.91; H, 8.13. Found: C, 65.88; H, 8.08.

Acknowledgment. R.R.S. thanks the National Science Foundation for support through Grant DMR 84-17818. We thank Prof. R. E. Cohen for helpful discussions and for use of equipment.

Registry No. $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; $Mo(CPr)(O\text{-}t\text{-}Bu)_3$, 91780-93-7; $W(C\text{-}t\text{-}Bu)(DIPP)_3$, 91229-76-4; $W(CEt)(O\text{-}t\text{-}Bu)_3$, 82228-88-4; $(t\text{-}BuO)_3W{\equiv}C(CH_2)_6C{\equiv}W(O\text{-}t\text{-}Bu)_3$, 119272-25-2; $(t\text{-}BuO)_3W{\equiv}C(CH_2)_5C{\equiv}W(O\text{-}t\text{-}Bu)_3$, 119272-26-3; $(t\text{-}BuO)_3W{\equiv}C(CH_2)_4C{\equiv}W(O\text{-}t\text{-}Bu)_3$, 119272-27-4; $(t\text{-}BuO)_3W{\equiv}C(CH_2)_2C{\equiv}W(O\text{-}t\text{-}Bu)_3$, 119272-28-5; $(t\text{-}BuO)_3Mo{\equiv}C(CH_2)_2C{\equiv}Mo(O\text{-}t\text{-}Bu)_3$, 119272-29-6; $W[C(t\text{-}Bu)C(CH_2)_6C][O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2]_3$, 119272-30-9; $Mo(C\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_3$, 82209-30-1; polycyclooctyne, 106989-28-0; cyclooctyne, 1781-78-8; 2,10-dodecadiyne, 31699-38-4; 1,9-cyclohexadecadiyne, 1697-71-8; 1,8-cyclotetradecadiyne, 1540-80-3; 2,8-decadiyne, 4116-93-2; 2,6-octadiyne, 764-73-8; 1,5-hexadiyne, 628-16-0.

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Photooxidation of Poly(vinyl chloride). 1. A Reexamination of the Mechanism

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Received April 14, 1988; Revised Manuscript Received December 5, 1988

ABSTRACT: Oxidation photoproducts formed by irradiation of poly(vinyl chloride) in the presence of air were investigated by FTIR spectroscopy. Specific chemical treatments were developed in order to identify the photoproducts. It was shown that only a few compounds were formed, including hydroperoxides, chlorinated ketones, acid chlorides, and carboxylic acids. A general scheme accounting for the mechanism of photooxidation of poly(vinyl chloride) is proposed.

Introduction

Despite the large number of papers dealing with the photodegradation of poly(vinyl chloride), it remains true that the carbonylated photoproducts observed by IR spectroscopy of aged films have not been totally identified. As a consequence, the mechanism of photooxidation is not established. In contrast, the initiation step involving absorption of light by poly(vinyl chloride) (PVC) has been extensively investigated. Even if some disagreement still exists concerning the nature of the absorbing chromophores responsible for the initiation step,[1] good potential candidates are postulated, for example, α-chlorinated short conjugated polyenes.[2,3]

The nature of the photoproducts responsible for the discoloration of PVC exposed to UV light has also been determined, and it is unambiguously agreed that the growing polyene sequences resulting from the well-known dehydrochlorination of poly(vinyl chloride) cause this discoloration. The length of these polyenes is readily characterized by UV spectrometry.[4] The quantum yield

0024-9297/89/2222-2576$01.50/0