tained by others in the polymerization of monomers in monolayers.[6,7]

We conclude that well-behaved monolayers are formed from this monomer and that UV-initiated polymerization takes place to give greatly stabilized and less compressable monolayer products containing polymer and residual monomer.

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Registry No. 1, 106133-27-1; 1 (homopolymer), 106158-81-0.

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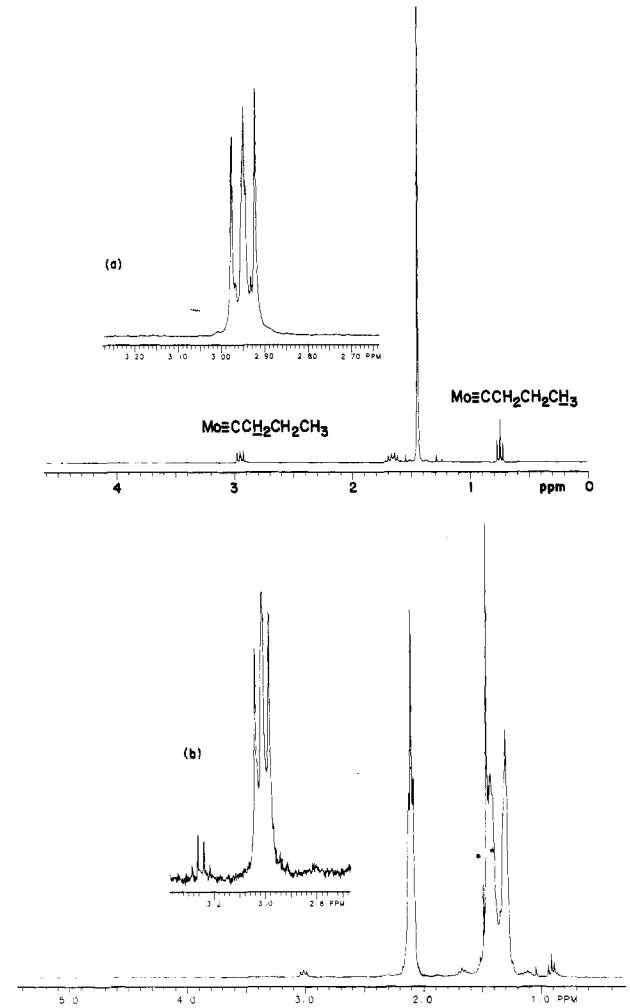

Figure 1. (a) ^{1}H NMR spectrum of (a)Mo($CCH_2CH_2CH_3$)-($OCMe_3$)$_3$ in C_6D_6; (b) ^{1}H NMR spectrum of Mo{[C-(CH_2)$_6$C]$_x$CPr}($OCMe_3$)$_3$ prepared by adding 15 equiv of cyclooctyne to the sample of Mo(CPr)($OCMe_3$)$_3$.

Ring-Opening Polymerization of Cyclooctyne

The ring-opening polymerization of cyclic olefins by olefin metathesis catalysts is now well-known,[1] and well-characterized catalysts are being discovered that allow one to prepare living polymers of this type.[2] Acetylene metathesis catalysts also are now well characterized.[3] The fact that their reactivity also can be altered greatly by the choice of metal (Mo or W) and the nature of the alkoxide ligand system created the possibility that an acetylene metathesis catalyst could be designed that would polymerize cyclooctyne (ring strain ~9 kcal mol^{-1}) by metathetical ring opening to give a living polymer. We report here a successful system of this type.

Acetylene metathesis catalysts that are highly active for the metathesis of internal acetylenes (e.g., W(CR)(O^tBu)$_3$[3a]) are not suitable for the controlled ring opening of cyclooctyne since the alkylidyne also will react with triple bonds in the growing chain. However, catalysts that are much less active are obtained simply by changing the metal from W to Mo.[3d] In fact, Mo(C^tBu)(O^tBu)$_3$ will not react with 3-heptyne, although it will react rapidly with 1-pentyne (eq 1).[3d] Mo(CPr)(O^tBu)$_3$ (**1a**) reacts only very slowly with

$$\mathrm{Mo(C^tBu)(O^tBu)_3 + PrC{\equiv}CH \rightarrow Mo(CPr)(O^tBu)_3 + {^t}BuC{\equiv}CH} \quad (1)$$

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^tBu)$_3$ in C_6D_6 (Figure 1a) are signals for the Mo≡C$CH_2CH_2CH_3$ protons at 2.95 ppm and the Mo≡C$CH_2CH_2CH_3$ protons at 0.74 ppm. Upon addition of 15 equiv of cyclooctyne these signals disappear and are replaced by those characteristic of what we believe to be Mo{[C(CH_2)$_6$C]$_x$CPr}(O^tBu)$_3$ (**1b**, Figure 1b); 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. The ^{13}C NMR spectrum (in C_6D_6) of the product made with 20 equiv of cyclooctyne exhibits a resonance at 80.4 ppm (among other expected resonances) that is shifted significantly from that for cyclooctyne at 94.5 ppm.[4] The range of chemical shifts for 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 formation of a polyene.

If only 1–5 equiv of cyclooctyne are added to Mo(CPr)(O^tBu)$_3$, all of the cyclooctyne is consumed, but not all of **1a** is converted into **1b**, and the relative amounts of **1a** and **1b** vary from one experiment to another. The failure to convert all of **1a** into **1b** could be due either to a fast reaction between cyclooctyne and **1a** relative to the rate of mixing or to a slower rate of reaction of cyclooctyne with **1a** than with **1b**. The latter would be surprising; **1a** was chosen as the initiator precisely so that it would react with cyclooctyne as rapidly as the propagating species **1b**. The former also is more consistent with different initial ratios of **1a** to **1b** being observed.

Over a period of 24 h the ratio of **1a** to **1b** slowly changes to reach what we believe to be equilibrium values (Table

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Table I
Equilibrium Values for Conversion of Mo(CPr)(O^{t}Bu)$_3$ (1a) into Mo{[C(CH$_2$)$_6$C]$_x$CPr}(O^{t}Bu)$_3$ (1b)[a]

equiv C_8H_{12}	% 1a	% 1b
1	40 (33[b])	60 (67[b])
2	23 (18[b])	77 (82[b])
3	15[b]	85[b]
4	11	89
8	5	95
10	5[b]	95[b]
12	4	96
20	2	98

[a] Cyclooctyne in 0.75 mL of C_6D_6 was added rapidly to a stirred solution of 10 mg of **1a** and *p*-dichlorobenzene (internal standard) in 1.5 mL of C_6D_6. The ratio of **1a** to **1b** 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.

Table II
GPC Studies on Polyethylene Prepared by Hydrogenation of 1b[a]

equiv C_8H_{12}	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ (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] 1a was hydrogenated at 60 psig of H_2 overnight in toluene employing $Rh(PPh_3)_3Cl$ 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 with a polydispersity from 4.4 to 7.0 and molecular weight as listed. 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.

I). We also know that if a sample of **1b** prepared from 15 equiv of cyclooctyne is mixed with an equal amount of **1a**, the amount of **1a** slowly decreases and an equilibrium mixture consisting of ~8% **1a** and 92% **1b** is established. The most plausible explanation of these findings is that cyclooctyne or some cyclic oligomer comes out of **1b** and reacts with **1a** until equilibrium is established between **1b** and **1a**. Examination of an ^1H NMR spectrum of **1b** (x = 15) at 120 °C showed no sign of cyclooctyne (≤2% estimated—there was some irreversible decomposition of the sample) or 1,9-cyclohexadecadiyne (the cyclic dimer of cyclooctyne). Therefore the equilibrium shown in eq 2 must lie far to the right. 1,9-Cyclohexadecadiyne *could* be responsible for the equilibration of **1a** and **1b** since upon adding it to **1a** **1b** is formed on the time scale of the equilibration of **1a** and **1b**.

$$\text{Mo\{[C(CH}_2\text{)}_6\text{C]}_x\text{CPr\}(O}^t\text{Bu)}_3 \underset{-(C_8H_{12})_n}{\overset{+(C_8H_{12})_n}{\rightleftharpoons}} \text{Mo\{[C(CH}_2\text{)}_6\text{C]}_y\text{CPr\}(O}^t\text{Bu)}_3 \quad (2)$$

If **1a** is added to 250, 350, and 500 equiv of cyclooctyne in toluene, then all monomer is consumed in seconds to give an insoluble gelatinous precipitate. Since all efforts to analyze this relatively insoluble polymer by standard GPC methods failed, it was hydrogenated under 60 psig of hydrogen at 60 °C to give a polymer whose T_g and melting point were close to those of polyethylene.[5] This polymer was analyzed by GPC in 1,2,4-trichlorobenzene at 145 °C. The results are shown in Table II. The most important finding is that $\bar{M}_n$ depends directly on the number of equivalents of cyclooctyne employed. Therefore we can say that the polymerization most likely is living, as all the evidence so far suggests. The relatively high polydispersities and low values of $\bar{M}_n$ (vs. theory for a perfect system) could be the result of the hydrogenation procedure, about which we know virtually nothing.[5] We will be searching for unambiguous methods of cleaving off the polymer chain (e.g., by reactions analogous to that shown in eq 1) and converting it under mild conditions into a soluble, easily characterized polymer.

To our knowledge this is the first report of ring-opening polymerization of cyclooctyne. We will be exploring the details of this reaction and will be searching for other catalysts that yield well-behaved living polymers.

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Registry No. Mo(CPr)(O*t*Bu)$_3$, 91780-93-7; Mo([C(CH$_2$)$_6$C]$_x$CPr)(O*t*Bu)$_3$, 106989-28-0.

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(4) The reaction appears to be extremely clean. Other resonances ascribable to the carbon atoms of the backbone are found at 18.78, 28.44, and 29.10 ppm. At this concentration of monomer other resonances can be observed for carbon atoms relatively close to the metal. The oligomer can be cleaved from the metal with phenylacetylene and fully characterized. Details will be reported in the full paper.
(5) We assume for the present that the catalyst is no longer active after the hydrogenation procedure. However, we do not know if the metal is still attached to the polymer (and therefore whether the GPC analysis is accurate or not) if the hydrogenation procedure leaves the polymer chain length unchanged.
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Stereocomplex Formation between Enantiomeric Poly(lactides)

It has been reported that a polymer–polymer complex can be formed upon mixing two polymers with different chemical compositions if a favorable interaction prevails between the different polymer chains as with complementary nucleic acids and proteins. The well-known interpolymer complexes include (1) a polyelectrolyte complex between polyanion and polycation,[1] (2) a hydrogen-bonding complex between a poly(carboxylic acid) and a polyether or polyol,[2] and (3) a charge-transfer complex between polymeric donor and acceptor.[3] However, only a few pairs

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