(7) Saegusa, T.; Ikeda, H.; Fujii, H. *Macromolecules* **1972**, *5*, 359.
(8) Witte, H.; Seeliger, W. *Liebigs Ann. Chem.* **1974**, 966.
(9) Ranganathan, N.; Storey, B. T. *J. Heterocycl. Chem.* **1980**, *17*, 1069.
(10) Ashby, E. C.; Lin, J.-J.; Goel, A. B. *J. Org. Chem.* **1978**, *43*, 183.
(11) (a) Lichtenberger, J.; Tritach, P. *Bull. Soc. Chim. Fr.* **1961**, 363. (b) Pavlisko, J. A.; Overberger, C. G. *J. Poly. Sci., Polym. Chem. Ed.* **1981**, *19*, 1621. *Kagaku Binran*; Maruzen: Tokyo, 1984; Vol. II, p 81.
(12) *Kagaku Binran*; Maruzen: Tokyo, 1984; Vol. II, p 81.

Synthesis and Properties of Poly(1-chloro-1-alkynes)

Toshio Masuda,* Toshio Yoshimura, Kazutaka Tamura, and Toshinobu Higashimura*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

Received December 18, 1986

ABSTRACT: 1-Chloro-1-hexyne, -1-octyne, and -1-decyne ($ClC{\equiv}CR$; R = n-C_4H_9, n-C_6H_{13}, and n-C_8H_{17}) polymerized with Mo catalysts [e.g., $MoCl_5$, $MoCl_5$—n-Bu_4Sn, and $Mo(CO)_6$—CCl_4—$h\nu$] in high yields to give new high molecular weight polymers ($\bar{M}_w$ ca. 2×10^5–2×10^6). 1-Chloro-1-hexadecyne, which has a long alkyl group (R = n-$C_{14}H_{29}$), polymerized similarly, whereas 1-chloro-3-propyl-1-hexyne, which has a *sec*-alkyl group [R = $CH(n\text{-}C_3H_7)_2$], hardly polymerized owing to the steric reason. The product polymers had the structure of $-(CCl{=}CR)_n-$ according to the spectroscopic analyses. The polymers of 1-chloro-1-hexyne, -1-octyne, and -1-decyne were white solids, while poly(1-chloro-1-hexadecyne) was a white rubbery material. They were totally soluble in many organic solvents, thermally fairly stable in air, amorphous, film-forming, electrically insulating, and nonparamagnetic.

Introduction

Polymers obtained from substituted acetylenes have alternating double bonds in the main chain and various groups in the side chain. Unlike the unsubstituted polyacetylene, many of them are stable to air and soluble in organic solvents. Catalysts based on groups 5 and 6 transition metals (Nb, Ta, Mo, and W) have been found effective in their synthesis.[2]

Many 1-halo-1-alkynes have been prepared so far.[3] The halogen atoms in 1-halo-1-alkynes are expected to have various effects such as inductive, mesomeric, and steric ones on the $C{\equiv}C$ bond, which has incited many organic chemists to study their reactivity.[4] In general, 1-chloro-1-alkynes are more stable in air at high temperature than other 1-halo-1-alkynes and hence are easier to handle.

To date, several polymers of 1-halo-1-alkynes have been known:[5] $ClC{\equiv}CPh$, $ClC{\equiv}C$—n-C_6H_{13}, $BrC{\equiv}CPh$, and $BrC{\equiv}C(CH_2)_4Br$. 1-Chloro-2-phenylacetylene polymerizes with only Mo catalysts to give a totally soluble high molecular weight polymer (MW ~ 1×10^6).[5a,5b] A recent short communication by us has revealed that 1-chloro-1-octyne also yields a high molecular weight polymer.[5c] In contrast, the polymer molecular weights of 1-bromo-1-alkynes ($BrC{\equiv}CPh$[5d] and $BrC{\equiv}C(CH_2)_4Br$[5e]) are no more than 1×10^4. Thus, it seems of great interest to examine the polymeriztion of various aliphatic 1-chloro-1-alkynes in detail.

The present paper deals with the synthesis and properties of poly(1-chloro-1-alkynes). New, high molecular weight polymers have been successfully synthesized from linear 1-chloro-1-alkynes (1-chloro-1-hexyne, -1-octyne, -1-decyne, and -1-hexadecyne) and their structure and properties have been clarified.

Results and Discussion

Polymerization of 1-Chloro-1-hexyne, 1-Chloro-1-octyne, and 1-Chloro-1-decyne. Table I gives results on the polymerization of three alkynes with C_4–C_8 alkyl groups, especially 1-chloro-1-octyne, in the presence of various catalysts. 1-Chloro-1-octyne polymerized only with Mo catalysts and did not yield any polymer (methanol-insoluble product) with W, Nb, Ta, Fe, or Ti catalysts. Difficulty of this monomer to polymerize with W catalysts coincides with the general tendency of 1-halo-1-alkynes,[5] and it should be associated with the electron-withdrawing property of the chlorine atom. It is known that Nb and Ta catalysts work well even for the polymerization of sterically crowded acetylenes as 1-(trimethylsilyl)-1-propyne.[2a] Hence, the result that 1-chloro-1-octyne does not polymerize with Nb or Ta catalysts is attributable to the electronic effect of the monomer. There has been no example of disubstituted acetylenes polymerizable with Ziegler catalysts (e.g., Fe and Ti catalysts); the present result for 1-chloro-1-octyne is consonant with it.

1-Chloro-1-hexyne, -1-octyne, and -1-decyne polymerize even with $MoCl_5$ alone in high yields under the conditions shown in Table I. However, use of n-Bu_4Sn, which reduces and/or alkylates $MoCl_5$, as cocatalyst accelerates the polymerizations (see below) and enhances the $\bar{M}_w$'s of polymers close to 1×10^6. The catalyst obtained by UV irradiation of the CCl_4 solution of $Mo(CO)_6$ effects still higher $\bar{M}_w$'s around 2×10^6. Thus, the $Mo(CO)_6$–CCl_4–$h\nu$ catalyst is suitable to accomplish very high molecular weight (the $MoCl_5$–cocatalyst systems, however, surpass it with regard to their higher activity and the ease of their preparation).

Table II shows what organometallics are useful as cocatalysts. As seen in the polymerization of 1-chloro-1-octyne, organometallics containing groups 4 and 5 main-group metals (Sn, Si, Sb, and Bi) generally give high yields of polymers with high molecular weights. In contrast, with organolithiums and -aluminum were formed appreciable amounts of methanol-soluble oligomers. This can be atttributed to their rather too strong reducing and alkylating ability (this is commensurate with the fact that $MoCl_5$ is excessively reduced to precipitate partly in the presence of these cocatalysts). Further, no polymer formed at all with the use of i-Bu_2AlH or 9-BBN, both of which have a metal–H bond.

For 1-chloro-1-hexyne, -1-octyne, and -1-decyne, groups 4 and 5 organometallic cocatalysts gave clearly better results than those in the absence of any cocatalyst; that is, both the yield and $\bar{M}_w$ of polymers tended to increase (Table II). In the case of organosilicons, no cocatalyst effect was observed unless they had a Si–H bond (e.g.,

0024-9297/87/2220-1734$01.50/0 © 1987 American Chemical Society

Table I
Polymerization of 1-Chloro-1-hexyne, 1-Chloro-1-octyne, and 1-Chloro-1-decyne by Various Catalysts[a]

no.	catalyst	monomer convn, %	polymer[b]		
			yield, %	$\bar{M}_w/10^{3c}$	$\bar{M}_n/10^{3c}$
		1-Chloro-1-hexyne			
1	$MoCl_5$	100	91	320	170
2	$MoCl_5$–n-Bu_4Sn	100	94	890	590
3	$Mo(CO)_6$–CCl_4–$h\nu^d$	97	81	2600	850
		1-Chloro-1-octyne			
4	$MoCl_5$	100	78	220	96
5	$MoCl_5$–n-Bu_4Sn	100	92	870	510
6	$Mo(CO)_6$–CCl_4–$h\nu^d$	90	85	1800[e]	740
7	WCl_6	10	0		
8	WCl_6–n-Bu_4Sn	16	0		
9	$W(CO)_6$–CCl_4–$h\nu^d$	9	0		
10	$NbCl_5$–n-Bu_4Sn^f	100[g]	0		
11	$TaCl_5$–n-Bu_4Sn^f	62[g]	0		
12	$Fe(acac)_3$–$3Et_3Al$	8	0		
13	$Ti(O$-n-$Bu)_4$–$4Et_3Al$	42[g]	0		
		1-Chloro-1-decyne			
14	$MoCl_5$	100	72	310	180
15	$MoCl_5$–n-Bu_4Sn	100	96	940	550
16	$Mo(CO)_6$–CCl_4–$h\nu^d$	96	92	1600	790

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0$ = 0.50 M, [Cat] = [n-Bu_4Sn] = 20 mM. [b] Polymer: methanol-insoluble product. [c] Determined by GPC. [d] Polymerized in CCl_4; $[M(CO)_6]$ = 10 mM. [e] $[\eta]$ = 6.96 dL/g (in toluene, 30 °C). [f] Polymerized at 80 °C. In the absence of n-Bu_4Sn, conversions were 100% ($NbCl_5$) and 84% ($TaCl_5$), and no polymer formed. [g] Product: cyclotrimers and/or linear oligomers.

Table II
Effects of Organometallic Cocatalysts on the Polymerization of 1-Chloro-1-hexyne, 1-Chloro-1-octyne, and 1-Chloro-1-decyne by $MoCl_5$[a]

cocatalyst	monomer convn, %	polymer[b]			
		yield, %	$\bar{M}_w/10^{3c}$	$\bar{M}_n/10^{3c}$	$[\eta]$, dL/g[d]
		1-Chloro-1-hexyne			
none	100	91	320	170	
n-Bu_4Sn	100	94	890	590	
Et_3SiH	100	98	1300	540	
Ph_3Sb	100	67	870	580	
Ph_3Bi	100	98	700	300	
n-BuLi	100	65	870	480	
Et_3Al	96	16	910	540	
		1-Chloro-1-octyne			
none	100	78	220	96	0.95
n-Bu_4Sn	100	92	870	510	2.80
Ph_4Sn	100	82	640	210	
Et_3SiH	100	93	1200	570	
Ph_3SiH	100	88	510	180	
Ph_3Sb	100	84	650	230	
Ph_3Bi	100	93	520	230	2.16
n-BuLi	100	48	820	390	3.78
t-BuLi	90	45	830	380	
Et_3Al	100	55	780	340	2.89
i-Bu_2AlH	100	0			
9-BBN[e]	96	0			
		1-Chloro-1-decyne			
none	100	72	310	180	
n-Bu_4Sn	100	96	940	550	
Et_3SiH	100	98	1400	560	
Ph_3Sb	100	82	720	360	
Ph_3Bi	100	98	560	330	
n-BuLi	27	18	870	440	
Et_3Al	84	28	730	260	

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0$ = 0.50 M, [Cat] = [Cocat] = 20 mM. [b] Polymer: methanol-insoluble product. [c] Determined by GPC. [d] Intrinsic viscosities measured in toluene at 30 °C. [e] 9-BBN: 9-borabicyclo[3.3.1]nonane.

Et_4Si); this should be due to the Si–C bond being stronger than those of Sn–C, etc.

Polymerization of 1-chloro-1-octyne proceeded in hydrocarbons and halogenated hydrocarbons (Table III).

Table III
Solvent Effects on the Polymerization of 1-Chloro-1-octyne by $MoCl_5$–n-Bu_4Sn[a]

solvent	monomer convn, %	polymer[b]		
		yield, %	$\bar{M}_w/10^{3c}$	$\bar{M}_n/10^{3c}$
toluene	100	92	870	510
cyclohexane	100	92	560	160
n-hexane	100	93	580	260
PhCl	100	93	400	190
CCl_4	100	92	430	170
$PhOCH_3$	100	88	240	100
$PhCOOCH_3$	44	0		
$PhCOCH_3$	0	0		

[a] Polymerized at 30 °C for 24 h; $[M]_0$ = 0.50 M, $[MoCl_5]$ = [n-Bu_4Sn] = 20 mM. [b] Polymer: methanol-insoluble product. [c] Determined by GPC.

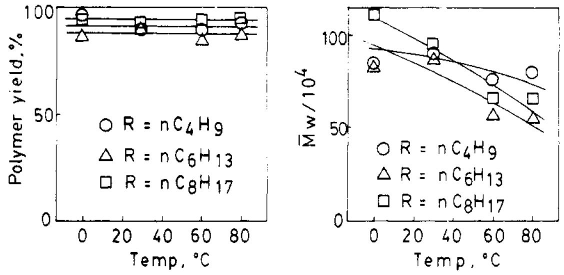

Figure 1. Temperature dependence of the polymerization of ClC≡CR by $MoCl_5$–n-Bu_4Sn (1:1) (in toluene, 24 h, $[M]_0$ = 0.50 M, $[MoCl_5]$ = 20 mM).

The polymer yield was hardly dependent on the kind of these solvents. However, the $\bar{M}_w$ changed to some extent with the kind of solvents, the highest value being attained in toluene. Regarding oxygen-containing solvents, 1-chloro-1-octyne gave a polymer in anisole, but not in more polar solvents like methyl benzoate and acetophenone. Thus, solvents such as toluene that have low polarity and dissolve catalysts and polymers well are favorable for polymerization.

Effects of temperature on the polymerization of the three 1-chloro-1-alkynes by $MoCl_5$–n-Bu_4Sn were studied (Figure 1). In the temperature range 0–80 °C, the polymer

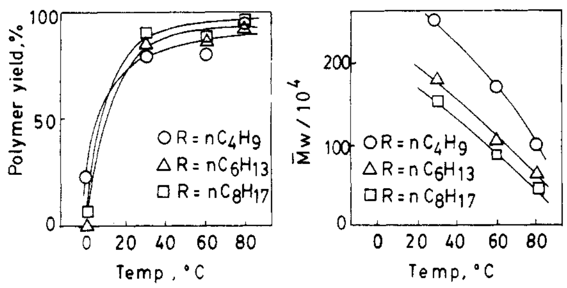

Figure 2. Temperature dependence of the polymerization of $ClC{\equiv}CR$ by $Mo(CO)_6$–CCl_4–$h\nu$ (in CCl_4, 24 h, $[M]_0 = 0.50$ M, $[Mo(CO)_6] = 10$ mM).

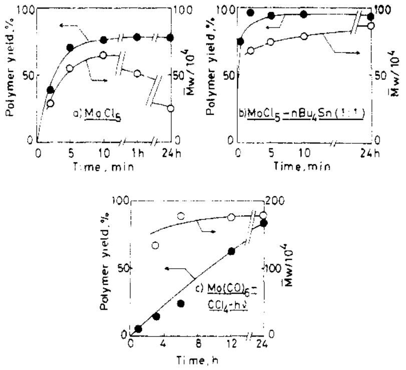

Figure 3. Time courses of the polymerization of 1-chloro-1-octyne by Mo catalysts (in toluene, 30 °C, $[M]_0 = 0.50$ M, $[MoCl_5] = 20$ mM, $[Mo(CO)_6] = 10$ mM).

yield was always as high as 90% with every monomer. On the other hand, the $\bar{M}_w$ tended to decrease with increasing temperature. Therefore, 0 or 30 °C is suitable to obtain high molecular weight polymers.

In the case of the $Mo(CO)_6$–CCl_4–$h\nu$ catalyst, polymers were formed in ~90% yields at 30 °C or above (Figure 2). The polymer yields at 0 °C were low or negligible with this catalyst. The $\bar{M}_w$ values at 30 °C were around 2×10^6 and decreased sharply with increasing temperature. Hence, 30 °C is the optimal temperature with the $Mo(CO)_6$–CCl_4–$h\nu$ catalyst.

1-Chloro-1-octyne polymerization proved to take a different time course for the yield and $\bar{M}_w$ of polymer depending on the kind of Mo catalysts (Figure 3): In the polymerization by $MoCl_5$ alone, all the monomer was consumed after 10 min, and the polymer yield at that time was 76%. The $\bar{M}_w$ of the polymer after 10-min reaction was 6.5×10^5, but it decreased to 2.2×10^5 after 24-h reaction owing to polymer degradation ($\bar{M}_w/\bar{M}_n$ was practically independent of polymerization time) (Figure 3a). With $MoCl_5$–n-Bu_4Sn as catalyst, the monomer consumption was completed within 2 min, and then the polymer yield was 96% and $\bar{M}_w$ was 6.8×10^5. No decrease of $\bar{M}_w$ was observed even after 24-h polymerization (Figure 3b). The polymerization by $Mo(CO)_6$–CCl_4–$h\nu$ proceeded much more slowly, but the polymer yield reached 85% after 24 h. The polymer formed possessed high $\bar{M}_w$ values (1.4×10^6–1.8×10^6) irrespective of conversion (Figure 3c).

It is clear from Figures 1–3 that $Mo(CO)_6$–CCl_4–$h\nu$ is less active than $MoCl_5$–n-Bu_4Sn but produces polymers having higher molecular weights.

Polymerization of 1-Chloro-1-hexadecyne ($ClC{\equiv}C$–n-$C_{14}H_{29}$). 1-Chloro-1-hexadecyne was chosen as a monomer which has a very long linear alkyl group, and its polymerization was examined. As seen in Table IV, suitable $MoCl_5$–cocatalyst systems afforded polymers in high yields (80–90%), while $Mo(CO)_6$–CCl_4–$h\nu$ achieved a very high molecular weight ($\bar{M}_w$ 1.8×10^6). Thus, the polymerization behavior of this monomer is very similar to that of 1-chloro-1-alkynes with a shorter alkyl group such as 1-chloro-1-octyne. The appearance and mechanical properties of the polymers, however, changed appreciably with the length of the alkyl group (see below).

Table IV
Polymerization of 1-Chloro-1-hexadecyne ($ClC{\equiv}C$-n-$C_{14}H_{29}$)[a]

no.	catalyst	monomer convn, %	polymer[b] yield, %	polymer[b] $\bar{M}_w/10^{3c}$	polymer[b] $\bar{M}_n/10^{3c}$
1	$MoCl_5$	100	70	150	56
2	$MoCl_5$–n-Bu_4Sn	100	87	630	320
3	$MoCl_5$–Et_3SiH	100	92	940	310
4	$MoCl_5$–Ph_3Sb	91	78	690	220
5	$MoCl_5$–Ph_3Bi	100	87	640	230
6	$MoCl_5$–n-$BuLi$	31	29	650	330
7	$MoCl_5$–Et_3Al	25	2		
8	$Mo(CO)_6$–CCl_4–$h\nu$[d]	80	72	1800	490

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 0.50$ M, [Cat] = [Cocat] = 20 mM. [b] Polymer: methanol-insoluble product. [c] Determined by GPC. [d] Polymerized in CCl_4; $[Mo(CO)_6] = 10$ mM.

Table V
Attempted Polymerization of 1-Chloro-3-propyl-1-hexyne [$ClC{\equiv}CCH(n$-$C_3H_7)_2$][a,b]

catalyst	temp, °C	monomer convn, %	polymer yield, %[c]
$MoCl_5$–n-Bu_4Sn	30	42	12[d]
$MoCl_5$–n-Bu_4Sn	60	77	3
$MoCl_5$–n-Bu_4Sn	80	86	0
$Mo(CO)_6$–CCl_4–$h\nu$[e]	30	0	0
WCl_6–n-Bu_4Sn	30	3	0
WCl_6–n-Bu_4Sn	60	19	0
$W(CO)_6$–CCl_4–$h\nu$[e]	30	0	0
$NbCl_5$–n-Bu_4Sn	80	16	0
$TaCl_5$–n-Bu_4Sn	80	6	0

[a] Polymerized in toluene for 24 h; $[M]_0 = 0.50$ M, [Cat] = [n-Bu_4Sn] = 20 mM. [b] The main product: linear oligomers. [c] Polymer: methanol-insoluble product. [d] $\bar{M}_w = 5000$ (GPC). [e] Polymerized in CCl_4; $[M(CO)_6] = 10$ mM.

Polymerization of 1-Chloro-3-propyl-1-hexyne [$ClC{\equiv}CCH(n$-$C_3H_7)_2$]. Polymerization of 1-chloro-3-propyl-1-hexyne, which possesses a *sec*-alkyl group, was attempted (Table V). Its polymer, however, could hardly be obtained with any catalysts. The yield of the polymer (methanol-insoluble product) produced with $MoCl_5$–n-Bu_4Sn at 30 °C was only ~10%, and the $\bar{M}_w$ was only 5×10^3. Though the monomer conversion was increased by increasing temperature, no polymer formed at all at high temperatures around 80 °C. All of W, Nb, and Ta catalysts failed to produce a polymer.

1-Chloro-2-phenylacetylene polymerizes in high yields with Mo catalysts.[5a,b] The very low polymerizability of 1-chloro-3-propyl-1-hexyne seems to be due to the steric effect of the *sec*-alkyl group being even larger than that of the phenyl group. Further, the fact that none of the 1-halo-1-alkynes including the present monomer gives any polymers with Nb or Ta catalysts suggests that these catalysts do not induce the polymerization of 1-halo-1-alkynes which has an electron-withdrawing halogen adjacent to the $C{\equiv}C$ bond.

Copolymerizations of 1-Chloro-1-decyne with 2-Decyne and 1-Chloro-2-phenylacetylene. In order to clarify the effect of chlorine on monomer reactivity, copolymerizations of 1-chloro-1-decyne with 2-decyne and 1-chloro-2-phenylacetylene by $MoCl_5$–n-Bu_4Sn were carried out. As is clear from Figure 4, the reactivity of 1-chloro-1-decyne in copolymerization is close to that of 2-decyne and is appreciably higher than that of 1-chloro-

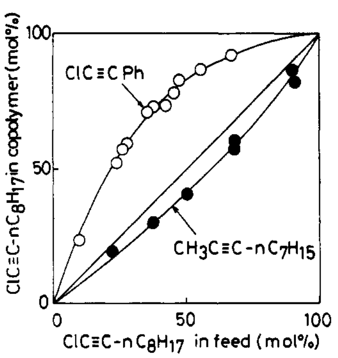

Figure 4. Composition curves for the copolymerizations of 1-chloro-1-decyne with 2-decyne and 1-chloro-2-phenylacetylene by $MoCl_5$–n-Bu_4Sn (1:1) (in toluene, 30 °C, $[M]_{0,total} = 0.50$ M, $[MoCl_5] = 5$–10 mM).

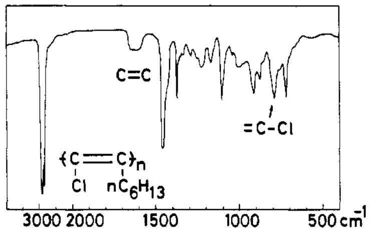

Figure 5. IR spectrum of poly(1-chloro-1-octyne) (KBr pellet, sample from Table I, no. 5).

Table VI
Elemental Analysis Data of Poly(1-chloro-1-alkynes)[a]

$-(C(Cl)=C(R))_n-$	R			
	n-C_4H_9	n-C_6H_{13}	n-C_8H_{17}	n-$C_{14}H_{29}$
C, %	61.43	66.40	69.63	74.17
	(61.81)	(66.43)	(69.55)	(74.82)
H, %	7.75	9.23	10.16	11.76
	(7.78)	(9.06)	(9.92)	(11.38)
Cl, %	30.02	24.34	20.48	13.63
	(30.41)	(24.51)	(20.53)	(13.80)

[a] Samples from Table I, no.s 2, 5, and 15, and Table IV, no. 2. Calculated values in parentheses.

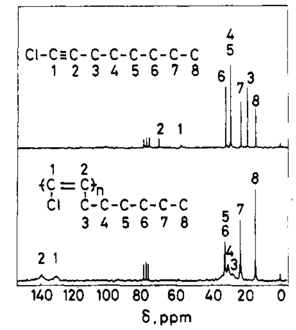

Figure 6. ^{13}C NMR spectrum of the monomer and polymer of 1-chloro-1-octyne ($CDCl_3$ solution, polymer sample from Table I, no. 4).

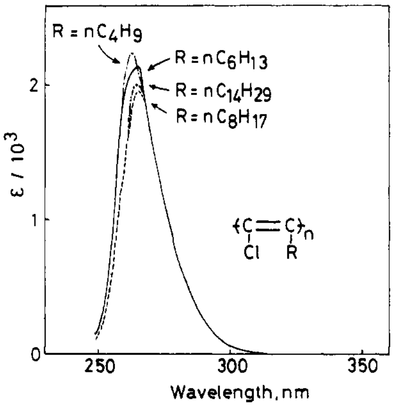

Figure 7. UV-visible spectra of poly(1-chloro-1-alkynes) (CCl_4 solution; samples from Table I, no.s 2, 5, and 15, and Table IV, no. 2).

2-phenylacetylene. The monomer reactivity ratios determined with the data in Figure 4 are as follows: $r_1 = 0.48 \pm 0.04$ and $r_2 = 1.12 \pm 0.12$ for the copolymerization of 1-chloro-1-decyne (M_1) with 2-decyne (M_2); $r_1 = 6.69 \pm 0.46$ and $r_2 = 0.52 \pm 0.06$ for the copolymerization of 1-chloro-1-decyne (M_1) with 1-chloro-2-phenylacetylene (M_2).

A general trend has been observed in copolymerization that, as an acetylene is sterically more crowded, it shows a lower relative reactivity.[6] It is reasonable to assume that the steric effects of 1-chloro-1-decyne and 2-decyne are similar to each other and smaller than that of 1-chloro-2-phenylacetylene. Then the present result can also be explained in terms of the steric factor of monomers, and it can be said that neither the electronic effect of chlorine nor the resonance effect of phenyl group plays an important role to the reactivity in copolymerization.

In general, copolymerization helps modify polymer properties. It is known that poly(1-chloro-1-decyne) is soft and ductile, whereas poly(1-chloro-2-phenylacetylene) is hard and brittle.[7a] When the copolymer composition was selected, mechanical properties of poly(1-chloro-1-decyne-*co*-1-chloro-2-phenylacetylene) could be arbitrarily controlled between those of the two homopolymers.[7b]

Polymer Structure. Values for the elemental analysis of poly(1-chloro-1-alkynes) were in satisfactory agreement with their theoretical ones (Table VI).

Figure 5 is the IR spectrum of poly(1-chloro-1-octyne). An absorption band due to C=C stretching is observed at 1660–1600 cm^{-1}. The band at 800 cm^{-1} is probably due to C–Cl stretching. Strong C–H stretching bands are seen at 2950 and 2850 cm^{-1}, while C–H deformation bands are at 1460 and 1380 cm^{-1}. The spectra of other poly(1-chloro-1-alkynes) were analogous.

In the ^{13}C NMR spectrum of the 1-chloro-1-octyne monomer are observed two acetylenic carbons at δ 69.8 and 57.2 (Figure 6). In the spectrum of its polymer, these peaks disappear, and instead two olefinic carbons appear at δ 136.8 and 129.0. The peaks of alkyl carbons in the side chain are seen in δ 35–15, an ordinary alkyl region. No other unexpected signals are observed. Other poly(1-chloro-1-alkynes) showed similar ^{13}C NMR spectra.

These IR and ^{13}C NMR data are compatible with the idea that the present polymers have the alternating double bond structure as shown in Figures 5 and 6. No information on the geometric structure of the main chain, however, could be obtained from these spectra.

As seen in Figure 7, the UV–visible spectra of poly(1-chloro-1-alkynes) show a small absorption maximum ($\epsilon \sim 2000$ M^{-1} cm^{-1}) around 280 nm and no absorption above 310 nm. These spectra correspond to the colorlessness of the polymers, indicating that alternating double bonds can conjugate only in a limited range owing to twisted main-chain conformations. The yellow color of poly(1-chloro-2-phenylacetylene)[5a] should result from conjugation of the main chain with phenyl group.

A logarithmic plot of intrinsic viscosities ($[\eta]$) vs. $\bar{M}_w$'s (data in Tables I and II) of poly(1-chloro-1-octyne) gave a good linear relationship. The least-squares treatment of the plot led to the equation

$$[\eta] = K\bar{M}_w^{\,a} \quad (a = 0.923,\ K = 1.11 \times 10^{-5}\ \mathrm{dL \cdot g^{-1}})$$

Exponent a in this equation is similar to those of other substituted polyacetylenes ($a = 0.9$–1.1)[2a] and larger than

Table VII
Several Properties of Poly(1-chloro-1-alkynes)[a]

$-(C(Cl)=C(R))_n-$	R: n-C_4H_9	n-C_6H_{13}	n-C_8H_{17}	n-$C_{14}H_{29}$
	Heat Treatment (In Air, 120 °C, 20 h)			
$\bar{M}_w/10^3$				
before	890	870	940	630
after	730	680	650	*b*
$\bar{M}_n/10^3$				
before	590	510	550	320
after	340	360	250	*b*
M_w/M_n				
before	1.5	1.7	1.7	2.0
after	2.1	1.9	2.6	
	Mechanical and Thermal Properties			
E,[c] MPa	800	430	70	
γ_B,[d] %	7	240	440	
T_g,[e] °C	190	150	90	−25
softening pt, °C	~310	~245	~225	~150
	Electric and Magnetic Properties			
σ,[f] S·cm^{-1}	2×10^{-17}	2×10^{-17}	3×10^{-16}	
spin density, g^{-1}		$<1 \times 10^{15}$		

[a] Samples from Table I, no.s 2, 5, and 15, and Table IV, no. 2. [b] The sample became partly insoluble after heat treatment. [c] E: Young's modulus (25 °C, data from ref 7). [d] γ_B: elongation at break (25 °C, data from ref 7). [e] T_g: glass transition temperature (data from ref 7). [f] σ: electrical conductivity (25 °C). [g] Unpaired-electron density (25 °C).

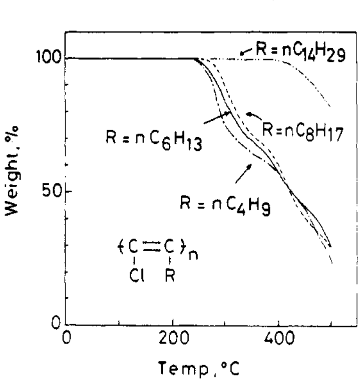

Figure 8. Thermogravimetric analysis of poly(1-chloro-1-alkynes) (in air, heating rate 10 °C/min; samples from Table I, no.s 2, 5, and 15, and Table IV, no. 2).

those of usual vinyl polymers (a = 0.5–0.8). Consequently, it proves that this polymer takes a fairly expanded conformation in solution.

Polymer Properties. Properties of the four kinds of polymers from 1-chloro-1-hexyne, -1-octyne, -1-decyne, and -1-hexadecyne are described (samples from Table I, no.s 2, 5, and 15, and Table IV, no. 2). The present polymers except poly(1-chloro-1-hexadecyne) had the form of white solid. Poly(1-chloro-1-hexadecyne) was a white rubbery material.

In general, these four polymers completely dissolved in hydrocarbons and halogenated hydrocarbons; their solvents are benzene, toluene, hexane, cyclohexane, CCl_4, $CHCl_3$, $(CH_2Cl)_2$, tetrahydrofuran, diethyl ether, etc., while their nonsolvents include ethyl acetate, methyl benzoate, acetone, acetophenone, acetonitrile, *N,N*-dimethylformamide, dimethyl sulfoxide, acetic acid, and ethanol.

Molecular weight changes by the heat treatment of poly(1-chloro-1-alkynes) in air at 120 °C for 20 h are shown in Table VII. The polymers of 1-chloro-1-hexyne, -1-octyne, and -1-decyne underwent only slight decreases in $\bar{M}_w$ and $\bar{M}_n$. They did not show any molecular weight change even when left in air at room temperature for 1 month. A major fraction of poly(1-chloro-1-hexadecyne) became insoluble in toluene after the heat treatment. Since this polymer has a long alkyl group and in turn a low glass transition temperature (T_g; see below), it is inferred that a small number of free radicals thermally formed react with alkyl chains of other molecules, leading to cross-linking.

As shown in Figure 8, the present polymers did not lose weight below 250 °C in the thermogravimetric analysis (TGA) in air. Interestingly, almost no weight loss was observed below 400 °C in poly(1-chloro-1-hexadecyne). This seems to be because, owing to the presence of the long alkyl chain, radicals thermally formed effect cross-linking which prevents the weight loss of the polymer.

When the above results are compared with those of other analogous polyacetylenes, it turns out that the polymer stability increases in the following order:[2a] $-[CH{=}C(n\text{-alkyl})]_n- < -[CCH_3{=}C(n\text{-alkyl})]_n- < -[CCl{=}C(n\text{-alkyl})]_n- < -[CCl{=}CPh]_n-$. Poly(1-alkynes) are easily oxidized in air and suffer significant molecular weight decrease even at room temperature; their weight loss in TGA starts at as low a temperature as 150 °C. Hence, it is evident that introduction of a chlorine atom at the C_1 position of 1-alkynes greatly enhances the polymer stability. Poly(2-alkynes) gradually degrade in air at room temperature. Thus, it is noteworthy that poly(1-chloro-1-alkynes) are clearly more stable than poly(2-alkynes) and somewhat less stable than poly(1-chloro-2-phenylacetylene) which is one of the most stable polyacetylenes.

The wide-angle X-ray diffraction diagram (Cu K_α radiation) of poly(1-chloro-1-octyne) consisted of one broad peak: diffraction angle (2θ) 23.6°, half-height width ($\Delta 2\theta$) 6.49°, $\Delta 2\theta / 2\theta$ 0.275. Hence, it is concluded that poly(1-chloro-1-octyne) and probably other poly(1-chloro-1-alkynes) as well are amorphous.

Colorless, transparent, free-standing films are accessible from the polymers of 1-chloro-1-hexyne, -1-octyne, and -1-decyne by casting their toluene solutions on a glass plate. Poly(1-chloro-1-hexadecyne) film was too soft and ductile at room temperature to retain its form.

Mechanical properties of these polymers remarkably change with alkyl chain length:[7a] Poly(1-chloro-1-hexyne) requires much force to elongate [has a high Young's modulus (E)] and breaks at a slight elongation [shows a small elongation at break (γ_B)] (see Table VII); i.e., it is hard and brittle. In contrast, poly(1-chloro-1-decyne), whose alkyl chain length is twice that of poly(1-chloro-1-hexyne), has a much lower Young's modulus and can be elongated by as much as 440%; i.e., it is soft and ductile. Poly(1-chloro-1-hexadecyne) is too soft and ductile at room temperature to measure its tensile properties.[7b]

The T_g's of the polymers of 1-chloro-1-hexyne, -1-octyne, and -1-decyne are 90 °C or above, and hence they are in the glass state at room temperature[7a] (Table VII). In general, polyacetylenes have the stiff main chain, and therefore their T_g's are high (usually ~200 °C).[2a] In contrast, the T_g of poly(1-chloro-1-hexadecyne) is below room temperature.[7b] To our knowledge, this polymer is the first example of polyacetylenes whose T_g is lower than room temperature. The softening point of poly(1-chloro-1-alkynes) decreased sharply with an increase of alkyl group length.

The electrical conductivities (σ) of the polymers of 1-chloro-1-hexyne, -1-octyne, and -1-decyne at 25 °C were 10^{-17}–10^{-16} S·cm^{-1}, lying in the insulator range ($<10^{-9}$ S·cm^{-1}). The unpaired-electron density of poly(1-chloro-1-octyne) at 25 °C was lower than the usual detection limit of 1×10^{15} spin·g^{-1} in the electron spin resonance (ESR) measurement. These electric and magnetic properties of

Table VIII
Synthesis and Properties of 1-Chloro-Substituted Acetylenes

R of ClC≡CR	yield, %	purity,[a] %	bp, °C (mmHg)	d_4^{20}, g/mL
n-C_4H_9[b]	60	99	74 (180)	0.923
n-C_6H_{13}[c]	56	>99	52 (12)	0.908
n-C_8H_{17}	65	>99	83 (8)	0.890
n-$C_{14}H_{29}$	53	99	110 (2)	0.869
$CH(n\text{-}C_3H_7)_2$	46	97	60 (15)	0.810
Ph[d]	75	>99	52 (3)	1.124

[a] By GC. [b] Lit. bp 65–67 °C (125 mmHg).[8] [c] Lit. bp 61–62 °C (17 mmHg), d_4^{20} 0.912 g/mL.[9] [d] Lit. bp 71 °C (16 mmHg), d_4^{18} 1.126 g/mL.[9]

the present polymers, along with their color, indicate that their main chain is considerably twisted.

Conclusions

High molecular weight polymers were obtained for the first time from aliphatic linear 1-chloro-1-alkynes by use of Mo-based catalysts. The product polymers are white, totally soluble in many organic solvents, film-forming, and thermally fairly stable. Their mechanical properties can be easily controlled by the alkyl chain length. Unique functions (e.g., membrane separation) of these polymers based on their special properties are now under investigation.

Experimental Section

Monomer Synthesis. 1-Chloro-1-alkynes, including 1-chloro-2-phenylacetylene, were prepared with reference to Brown's method.[8] As an example, the procedure for synthesizing 1-chloro-1-octyne is described in detail: The reaction was carried out in a 1-L three-necked flask fitted with a motor stirrer, reflax condenser, nitrogen inlet, and pressure-equalized dropping funnel. After flushing the system with dry nitrogen, the flask was charged with 1-octyne (0.40 mol, 44 g, 59 mL) and tetrahydrofuran (THF, 150 mL). After the flask had been cooled –50 °C, a hexane solution of n-butyllithium (1.6 M, 0.40 mol, 250 mL) was added dropwise from the dropping funnel, and stirring was continued further for 1 h. Then a THF solution of p-toluenesulfonyl chloride (0.40 mol, 76 g in 100 mL of THF) was added dropwise while the reaction mixture was kept at –50 °C. The reaction was completed by stirring at 0 °C for 1 h, which was confirmed by gas chromatography (GC). Water (10 mL) was carefully added, the reaction mixture was washed with water, and the water phase was extracted with hexane. The combined organic phase was dried over anhydrous sodium sulfate overnight, low volatiles were evaporated, and the product was distilled twice from calcium hydride.

Yields and properties of 1-chloro-1-alkyne monomers are shown in Table VIII. 1-Chloro-1-decyne, -1-hexadecyne, and -3-propyl-1-hexyne are new compounds. The other 1-chloro-1-alkynes in Table VIII had been prepared by various methods;[3] the present process, however, seems the most convenient to carry out on a laboratory scale. Though molecular chlorine can be used to chlorinate 1-alkynyllithiums,[10] use of p-toluenesulfonyl chloride is by far easier and safer. 3-Propyl-1-hexyne, the starting compound for the synthesis of 1-chloro-3-propyl-1-hexyne, was prepared by the literature method[11] (bp 58 °C/50 mmHg, yield 55%).

Catalyst Preparation and Polymerization. Transition metal compounds and organometallic cocatalysts were commercially obtained and used without further purification. Toluene as polymerization solvent was washed with dilute sulfuric acid, aqueous sodium hydroxide solution, and water, dried over calcium chloride overnight, and distilled twice from calcium hydride. Other polymerization solvents were purified similarly.

In general, catalyst preparation and polymerization were carried out under dry nitrogen in baked flasks equipped with a three-way stopcock. Catalysts composed of a transition metal chloride and an organometallic cocatalyst were allowed to stand (aged) in solution at polymerization temperature for 15 min just before use. Metal carbonyl based catalysts were prepared by UV irradiation of a CCl_4 solution of a metal carbonyl with a 200-W high-pressure Hg lamp from a distance of 5 cm at 30 °C for 1 h.

The polymerization procedure is explained by the following typical example (see Table I, no. 5, for the results): In a 10-mL flask were placed 1-chloro-1-octyne (6.0 mmol, 0.87 g, 0.95 mL), dodecane (0.35 mL; as internal standard of GC), and toluene (4.7 mL). In a 30-mL flask, $MoCl_5$ (0.20 mmol, 55 mg) and n-Bu_4Sn (0.20 mmol, 69 mg, 66 μL) were dissolved in toluene (5.0 mL), and the solution was left at 30 °C for 15 min. Then 5 mL of the monomer solution was added to the catalyst solution at 30 °C. After 24 h, polymerization was terminated by adding a mixture (3 mL) of toluene and methanol (volume ratio 4:1), and monomer conversion was determined by GC (silicone DC 3 m, 150 °C). The reaction mixture was diluted with toluene (20 mL) and poured into methanol (500 mL) under stirring. The precipitated polymer was filtered off and dried. Polymer yield was determined by gravimetry.

Polymer Characterization. $\bar{M}_w$ and $\bar{M}_n$ values of polymers were tentatively determined by GPC. GPC curves were observed with a Jasco Trirotar chromatograph (eluent, $CHCl_3$; columns, Shodex A802, A804, A806, and A807 polystyrene gels; polystyrene calibration). $[\eta]$ values of polymers were measured in toluene at 30 °C. Elemental analysis was carried out at the Laboratory for Organic Elemental Microanalysis, Kyoto University. IR and ^{13}C NMR spectra were recorded on a Shimadzu IR435 spectrophotometer and a Jeol FX90Q spectrometer, respectively. Thermogravimetric analysis was conducted with a Shimadzu DT20B thermal analyzer.

Acknowledgment. We thank Dr. Kazuhiko Takai for discussion on monomer synthesis. Thanks are also due to Dr. Takeji Hashimoto and Dr. Takashi Kawamura for the measurements of X-ray diffraction and ESR, respectively. This research was partly supported by the Grant-in-Aid on Special Project Research for "Organic Thin Films for Information Conversion" from the Ministry of Education, Science and Culture.

Registry No. $HC{\equiv}CC_8H_{17}$, 100858-78-4; $H_3CC{\equiv}CC_7H_{15}$, 2384-70-5; ClC≡CPh, 1483-82-5; $C_4H_9C{\equiv}CCl$ (homopolymer), 100858-76-2; $C_6H_{13}C{\equiv}CCl$ (homopolymer), 100858-77-3; C_8H_{17}-C≡CCl (homopolymer), 100858-79-5; $C_{14}H_{29}C{\equiv}CCl$ (homopolymer), 108711-62-2; $(C_3H_7)_2CHC{\equiv}CCl$ (homopolymer), 108711-64-4; ClC≡CPh (homopolymer), 81953-16-4; $MoCl_5$, 10241-05-1; $Mo(CO)_6$, 13939-06-5; CCl_4, 56-23-5; Bu_4Sn, 1461-25-2; Et_3SiH, 617-86-7; Ph_3Sb, 603-36-1; Ph_3Bi, 603-33-8; BuLi, 109-72-8; Et_3Al, 97-93-8; Ph_4Sn, 595-90-4; Ph_3SiH, 789-25-3; t-BuLi, 594-19-4.

References and Notes

(1) Part 11 of "Polymerization of Aliphatic Acetylenes". Part 10: Masuda, T.; Takahashi, T.; Niki, A.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 809.

(2) For reviews, see: (a) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1986**, *81*, 121. (b) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51.

(3) See: Delavarenne, S. Y.; Viehe, H. G. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; Chapter 10.

(4) E.g.: Nelson, D. J.; Blue, C. D.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 4913.

(5) (a) Masuda, T.; Kuwane, Y.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1043. (b) Masuda, T.; Yamagata, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 126. (c) Masuda, T.; Tamura, K.; Higashimura, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1615. (d) Kawasaki, M.; Masuda, T.; Higashimura, T. *Polym. J. (Tokyo)* **1983**, *15*, 767. (e) Yamagata, M.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2275.

(6) Masuda, T.; Yoshizawa, T.; Okano, Y.; Higashimura, T. *Polymer* **1984**, *25*, 503.

(7) (a) Masuda, T.; Tang, B.-Z.; Tanaka, A.; Higashimura, T. *Macromolecules* **1986**, *19*, 1459. (b) Tang, B.-Z.; Masuda, T.; Tanaka, A.; Higashimura, T., unpublished results.

(8) Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975; p 184.

(9) Truchet, R. *Ann. Chim. (Paris)* **1931**, *16*, 309.

(10) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981; p 67.

(11) Quillinan, A. J.; Scheinmann, F. *Org. Synth.* **1978**, *58*, 1.