Synthesis of High Polymers from Substituted Acetylenes: Exploitation of Molybdenum- and Tungsten-Based Catalysts

TOSHIO MASUDA* and TOSHINOBU HIGASHIMURA

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

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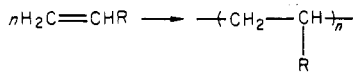
Unlike vinyl polymers **1**, acetylenic polymers **2** possess alternating double bonds along the main chain.



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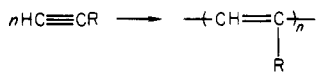

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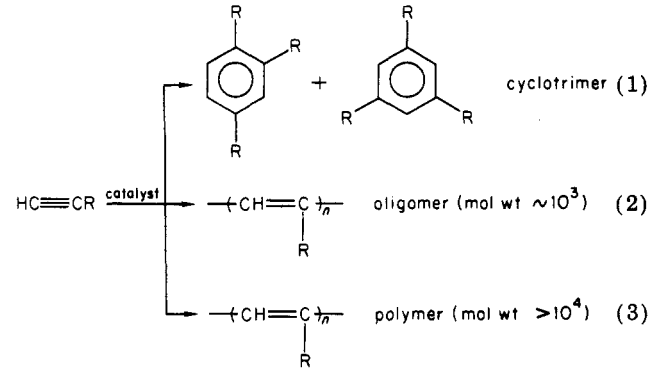
This structure often endows acetylenic polymers with the following characteristics:[1] (i) conductivity (semiconductivity), (ii) paramagnetism, (iii) migration and transfer of energy, (iv) color, and (v) chemical reactivity and complex formation ability. Because of these unique properties, acetylenic polymers seem promising as specialty polymer materials, which might have unique and useful functions.

Vinyl polymers have been extensively investigated and are manufactured in large quantities. On the other hand, the study on the polymerization of acetylenes has been much less developed, mainly due to the low polymerizability of acetylenes in the presence of conventional radical and ionic catalysts.[1]

Unsubstituted acetylene has been polymerized successfully to a polymer film by use of Ziegler catalysts such as a mixture of titanium tetra-*n*-butoxide and triethylaluminum (1:4) [$Ti(O\text{-}n\text{-}Bu)_4{\cdot}4Et_3Al$].[2] The high conductivity of doped polyacetylenes was first observed by Shirakawa et al. several years ago,[3] and now research on the applications of polyacetylene to such uses as polymer batteries and solar cells are in progress in many laboratories.

The polymerization of substituted acetylenes has been attempted by various methods: heat, light, radiation, and radical, ionic or transition-metal catalysts.[1a,c] In most cases, however, the products are not high polymers but linear oligomers and/or cyclotrimers[1a] (eq 1–3). In general, Ziegler catalysts give the best results with substituted acetylenes. For example, a mixture of iron(III) acetylacetonate and triethylaluminum (1:3) [$Fe(acac)_3{\cdot}3Et_3Al$] polymerizes *prim*- or *sec*-alkylacetylenes and phenylacetylene in high yields.[4] To the best of our knowledge, however, Ziegler catalysts do not yield high polymers from sterically hindered acetylenes such as *tert*-butylacetylene and disubstituted acetylenes ($R_1C{\equiv}CR_2$). Thus, the study



of substituted acetylenes remains chiefly on the synthesis of high-molecular-weight polymers.

About a decade ago, we examined various transition-metal halides as catalysts for the polymerization of phenylacetylene to find eventually that WCl_6 and $MoCl_5$ (group 6 transition metal chlorides) are particularly effective.[5] Since then we have been concerned with the polymerization of substituted acetylenes, especially sterically hindered ones, and with the exploitation of novel catalysts. The present polymerization is intimately associated with organometallic chemistry, and the polymers formed are finding some interesting applications. This Account presents a review of our research in the context of the current literature.

Polymerization of Aromatic Acetylenes

Phenylacetylene. We demonstrated for the first time that WCl_6 polymerizes phenylacetylene in high yield, and $MoCl_5$ polymerizes in moderate yield (Table I, no. 1, 2).[5,6] The number-average molecular weight ($\bar{M}_n$) of the polymer formed with WCl_6 was about 15 000, which was the highest among those reported for poly(phenylacetylene) at that time.

Aromatics, halogenated hydrocarbons, and ethers are useful polymerization solvents. The reaction proceeds faster in less polar media (e.g., CCl_4 > benzene ≃ toluene > 1,2-dichloroethane). The polymerization with WCl_6 is significantly accelerated in the presence of tetraphenyltin (Ph_4Sn) as a cocatalyst (WCl_6:Ph_4Sn =

Toshio Masuda is Associate Professor of Polymer chemistry at Kyoto University. He was born in 1944, received his Ph.D from Kyoto University in 1973, and did postdoctoral work with Professor John K. Stille at the University of Iowa.

Toshinobu Higashimura is Professor of Polymer Chemistry at Kyoto University. Born in 1929, he received his B.S. and Ph.D. degrees from Kyoto University before joining the faculty in 1956. He received the Award of the Society of Polymer Science Japan in 1965.

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Table I
Polymerization of Phenylacetylene[a]

no.	catalyst	solvent	time, h	polymer yield, %	$10^{-3}\bar{M}_n$
1	WCl_6	toluene	1	>90	10-15
2	$MoCl_5$	toluene	1	30-60	6
3	WCl_6·Ph_4Sn	toluene	1/20	~100	10-15
4	WCl_6·Ph_4Sn	1,4-dioxane	24	60-90	90-100
5	$W(CO)_6$-CCl_4-$h\nu$	CCl_4	24	>90	80-100
6	$Mo(CO)_6$-CCl_4-$h\nu$	CCl_4	24	~10	13

[a] Polymerized at 30 °C, $[M]_0$ = 1.0 M, [Cat.] = 10-20 mM.

Table II
Polymerization of Aromatic Acetylenes

monomer	catalyst activity[a]						polymer	
	WCl_6	WCl_6·Ph_4Sn	$W(CO)_6$-CCl_4-$h\nu$	$MoCl_5$	$MoCl_5$·Ph_4Sn	$Mo(CO)_6$-CCl_4-$h\nu$	$10^3\bar{M}_n$[b]	color
HC≡CPh	H	H	H	L	L	L	100	auburn to yellow
HC≡C$\beta$$C_{10}H_7$							150	auburn to orange
CH_3C≡CPh	O	H	O	O	O	O	5	white
PhC≡CPh							insol	yellow
ClC≡CPh	O	O	O	O	H	H	2000 ($\bar{M}_w$)	light yellow
BrC≡CPh							15	light yellow

[a] Polymer yield: (H) high, (L) low, (O) zero to negligible. [b] Maximum molecular weights.

1:1) (Table I, no. 3).[7] It was proved that the W(VI) of the catalyst is reduced to a W(IV) by Ph_4Sn. This catalyst system will be denoted by WCl_6·Ph_4Sn in the following discussions.

Poly(phenylacetylenes) with higher molecular weights can be obtained by two methods. One is to use solvents containing active hydrogens such as 1,4-dioxane, cyclohexene, and tetralin[8] (e.g., Table I, no. 4). The active hydrogens of these solvents seem to prevent polymer degradation proceeding by a radical mechanism and/or modify the nature of the active species. Another method of enhancing the molecular weight is as follows:

A catalyst obtained by UV irradiation of $W(CO)_6$ in carbon tetrachloride is capable of polymerizing phenylacetylene[9] (Table I, no. 5). The molecular weight reaches about 1×10^5. $Mo(CO)_6$ is much less effective and $Cr(CO)_6$ is inactive, though they are also group 6 transition metal carbonyls. The polymerization using $W(CO)_6$ and $Mo(CO)_6$ does not proceed without UV irradiation or in a hydrocarbon solvent instead of carbon tetrachloride, which indicates that both UV irradiation and carbon tetrachloride are indispensable to the formation of the active species. Hence, this catalyst system is designated $M(CO)_6$–CCl_4–$h\nu$ (M = W, Mo). It is noteworthy that the $W(CO)_6$–CCl_4–$h\nu$ system metathesizes olefins[10] (vide infra).

The poly(phenylacetylene) obtained with the W-based catalysts (WCl_6, WCl_6·Ph_4Sn, and $W(CO)_6$–CCl_4–$h\nu$) has a trans-rich structure, whereas a cis-rich structure is formed by the corresponding Mo catalysts ($MoCl_5$, $MoCl_5$·Ph_4Sn, and $Mo(CO)_6$–CCl_4–$h\nu$).[6] These polymers are amorphous and totally soluble in aromatic and halogenated hydrocarbons. On the other hand, $Fe(acac)_3$·$3Et_3Al$, a Ziegler catalyst, produces a crystalline insoluble poly(phenylacetylene) that possesses a practically all-cis structure.[11]

Table III
Polymerization of 1-Chloro-2-phenylacetylene[a]

catalyst (concn, mM)	solvent	polymer yield, %	$10^{-3}\bar{M}_w$
$Mo(CO)_6$-CCl_4-$h\nu$ (10)	CCl_4	80	2030
$MoCl_5$ (20)	toluene	5	
$MoCl_5$·n-Bu_4Sn (20)	toluene	91	740
$MoCl_5$·Et_3SiH (20)	toluene	75	690
$MoCl_5$·Ph_3Bi (20)	toluene	83	960

[a] Polymerized at 30 °C for 24 h, $[M]_0$ = 1.0 M.

Phenylacetylene Derivatives. The polymerizabilities of phenylacetylene and its several derivatives are shown in Table II. Similarly to phenylacetylene, β-naphthylacetylene is polymerized by all of the six Mo- and W-based catalysts.[12] In contrast, 1-phenyl-1-propyne[13] and diphenylacetylene,[14] being disubstituted acetylenes, can be polymerized only by WCl_6·Ph_4Sn. Ziegler catalysts polymerize β-naphthylacetylene[15] but not the latter two monomers.

1-Chloro-2-phenylacetylene[9a,16] and 1-bromo-2-phenylacetylene[17] can only be polymerized by Mo-based catalysts, probably because of the electron-withdrawing properties of the halogen atoms (Table II). It is of great interest that $Mo(CO)_6$–CCl_4–$h\nu$ yields poly(1-chloro-2-phenylacetylene) with a weight-average molecular weight[18] ($\bar{M}_w$) of up to two million[16a] (Table III). Mixed

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(8) Masuda, T.; Takahashi, T.; Yamamoto, K.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2603.
(9) (a) Masuda, T.; Kuwane, Y.; Yamamoto, K.; Higashimura, T. *Polym. Bull.* **1980**, *2*, 823. (b) Masuda, T.; Yamamoto, K.; Higashimura, T. *Polymer* **1982**, *23*, 1663.
(10) (a) Krausz,; P.; Garnier, F.; Dubois, J.-E. *J. Am. Chem. Soc.* **1975**, *97*, 437. (b) Agapiou, A.; McNelis, E. *J. Chem. Soc., Chem. Commun.* **1975**, 187.
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(13) Sasaki, N.; Masuda, T.; Higashimura, T. *Macromolecules* **1976**, *9*, 664.
(14) Masuda, T.; Kawai, H.; Ohtori, T.; Higashimura, T. *Polym. J.* **1979**, *11*, 813.
(15) Simionescu, C. I.; Dumitrescu, S.; Percec, V. *Polym. J.* **1976**, *8*, 139.
(16) (a) Masuda, T.; Kuwane, Y.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1043. (b) Masuda, T.; Yamagata, M.; Higashimura, T. *Macromolecules*, in press.
(17) Yamagata, M.; Masuda, T.; Higashimura, T., *J. Polym. Sci., Polym. Chem. Ed.*, in press.

Table IV
Polymerization of C_6 Alkynes

monomer	catalyst activity[a] $MoCl_5$	WCl_6	$MoCl_5$·Ph_4Sn	WCl_6·Ph_4Sn	$Mo(CO)_6$–CCl_4–$h\nu$	$W(CO)_6$–CCl_4–$h\nu$	relative activity	polymer $10^{-3}\bar{M}_n$[b]	polymer color
HC≡C–CH₂–C≡C–CH₃	L	L	L	H	L	H	W > Mo	4	orange
HC≡C–CH(CH₃)–C≡C–CH₃	L	H	L	H	L	H	W > Mo	10	yellow
HC≡C–C(CH₃)₂–C≡C–CH₃	H	H	H	H	H	H	Mo ≃ W	20	light yellow
HC≡C–C(CH₃)(CH₃)–C≡C–CH₃	H	H	H	H	H	H	Mo > W	400	white
CH₃–C≡C–CH₂–C≡C–CH₃	O	O	H	H	O	O	Mo > W	500	white
CH₃–C≡C–CH(CH₃)–C≡C–CH₃	O	O	L	L	O	O	W > Mo	insol	white
CH₃–C≡C–CH₂–C(CH₃)–C≡C–CH₃	O	O	L	H	O	O	W >> Mo	10	white

[a] Polymer yield: (H) high, (L) low, (O) zero to negligible. [b] Maximum molecular weights.

catalysts of $MoCl_5$ with suitable organometallics are also effective for the polymerization of 1-chloro-2-phenylacetylene, while $MoCl_5$ alone yields mainly oligomers.[16b]

Large differences exist in the maximum molecular weight of the polymers of aromatic acetylenes[6,12-17] (Table II). The polymers from the disubstituted acetylenes are white or only slightly colored. The electrical conductivities of all these polymers lie in the insulator range[19] ($\sigma = 10^{-18}$–10^{-14} S·cm^{-1}). The unpaired electron density of poly(phenylacetylene) is 10^{17}–10^{18} spins·g^{-1} and those of poly(1-phenyl-1-propyne) and poly(1-chloro-2-phenylacetylene) are practically undetectable (<10^{15} spins·g^{-1}). These findings contrast with the fact that polyacetylene is black, semiconductive ($\sigma = 10^{-9}$–10^{-5} S·cm^{-1}),[3] and paramagnetic (10^{19} spins·g^{-1}).[20] The properties of the polymers of disubstituted acetylenes should be closely related to their highly twisted, sterically crowded main chain in which little conjugation of the double bonds can be expected.

Polymerization of Aliphatic Acetylenes

Since the Mo- and W-based catalysts were found effective for aromatic acetylenes, aliphatic acetylenes were then polymerized with these catalysts. To know the structure–reactivity relationship, we employed all the seven isomers of aliphatic acetylenes having molecular formula C_6H_{10} (referred to as C_6 alkynes).[21] Table IV leads to the following conclusions: (i) every Mo or W catalyst polymerizes all the terminal alkynes, (ii) $MoCl_5$·Ph_4Sn and WCl_6·Ph_4Sn are sufficiently active to polymerize the internal alkynes, and (iii) the relative activity of a Mo catalyst to its W counterpart depends upon the monomer but not on its ligand (i.e., chloride or carbonyl). It is to be noted that Ziegler catalysts can polymerize neither *tert*-butylacetylene nor the internal alkynes.

Characteristics regarding the molecular weight and properties of the seven C_6-alkyne polymes are as follows.[21] Poly(*tert*-butylacetylene) and poly(2-hexyne) have prominently high molecular weights among them (Table IV). This indicates that an adequate steric hindrance in the monomer is favorable or rather necessary for the formation of high polymers. Most polymers from the terminal akynes are colored, whereas those from the internal alkynes are white because the main chains are considerably twisted. All these polymers showed very low electrical conductivities (10^{-18} S·cm^{-1} or below). The unpaired electron densities of the polymers from *tert*-butylacetylene and the internal alkynes were too low to detect (<10^{15} spins·g^{-1}).

As described above, *tert*-butylacetylene and 2-hexyne form very high polymers. Examples of their polymerization are shown in Table V. *tert*-Butylacetylene can

Table V
Polymerization of *tert*-Butylacetylene and 2-Hexyne[a]

monomer	catalyst (concn, mM)	polymer yield, %	
HC≡C-*t*-Bu	$MoCl_5$ (20)	100	301 ($\bar{M}_n$)
HC≡C-*t*-Bu	WCl_6 (20)	92	54 ($\bar{M}_n$)
2-hexyne	$MoCl_5$·Ph_4Sn (30)	88	1120 ($\bar{M}_w$)
2-hexyne	WCl_6·Ph_4Sn (30)	57	200 ($\bar{M}_w$)

[a] Polymerized in toluene at 30 °C for 24 h, $[M]_0$ = 1.0 M.

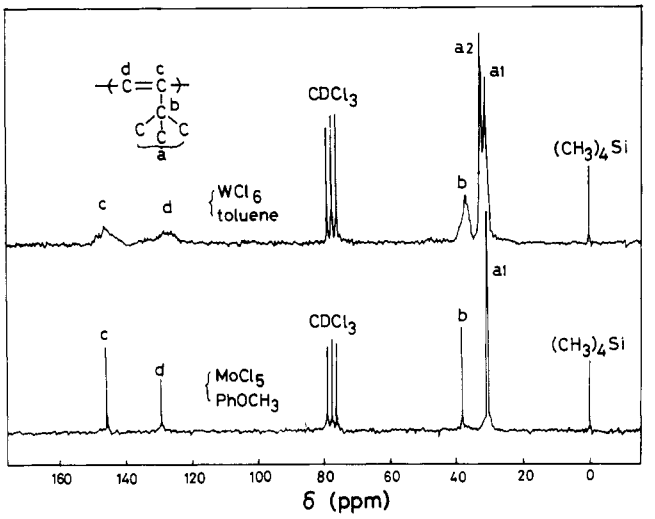


Figure 1. ^{13}C NMR spectra of two types of poly(*tert*-butylacetylenes) prepared under different conditions.[22b]

(18) It is difficult to determine a $\bar{M}_n$ of a million or above. The $\bar{M}_w$ of a polymer formed by homogeneous polymerization is usually about twice its $\bar{M}_n$.

(19) The insulator, semiconductor, and conductor are defined as those that possess specific conductivities (σ) of <10^{-9}, 10^{-9}–10^{2}, and > 10^{2} S·cm^{-1}, respectively.

(20) For example, see: Snow, A.; Brant, P.; Weber, D.; Yang, N.-L. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 263.

(21) Masuda, T.; Kawasaki, M.; Okano, Y.; Higashimura, T. *Polym. J.* **1982**, *14*, 371.

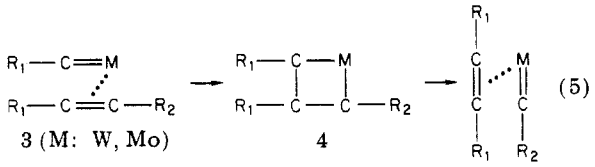
be polymerized by both $MoCl_5$ and WCl_6; the former is more active.[22] The geometric structure of poly(*tert*-butylacetylene) can be evaluated by ^{13}C NMR spectroscopy (Figure 1). Poly(*tert*-butylacetylene) obtained with $MoCl_5$ in oxygen-containing solvents (anisole, acetophenone, etc.) generally possesses the all-cis structure. It is important that the geometric structure can be regulated by such a judicious choice of polymerization conditions. 2-Hexyne is polymerized by $MoCl_5$·Ph_4Sn and WCl_6·Ph_4Sn, the former catalyst giving a very high polymer.[23] Higher 2-alkynes (2-heptyne to 2-decyne) are similarly polymerized. On the other hand, the polymerization of symmetrical dialkylacetylenes (3-hexyne, 4-octyne, and 5-decyne) is more effectively catalyzed by WCl_6·Ph_4Sn than $MoCl_5$·Ph_4Sn to produce insoluble polymers.[24]

Relationship to Olefin Metathesis and Polymerization Mechanism

The olefin metathesis reaction expressed by eq 4 proceeds best in the presence of W- and Mo-based catalysts.[25] It is now generally accepted that metal

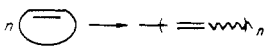
$$2R_1{-}C{\equiv}C{-}R_2 \rightleftarrows R_1{-}C{\equiv}C{-}R_1 + R_2{-}C{\equiv}C{-}R_2 \quad (4)$$

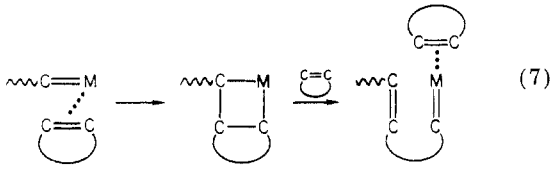
carbenes (**3**) and metallacyclobutanes (**4**) mediate this reaction as shown in eq 5. If a cycloolefin is used for



(5)

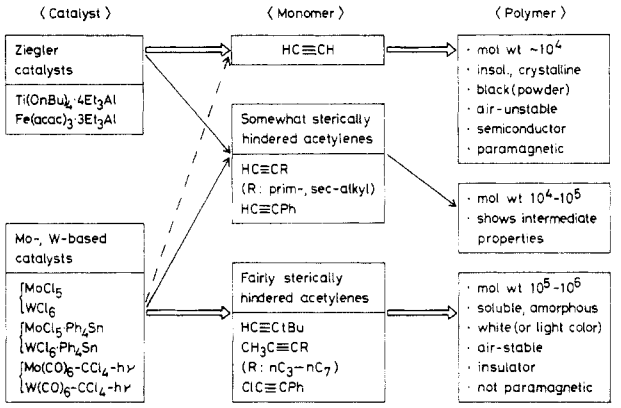
this reaction, a polymer is formed[26] (eq 6; called metathesis polymerization). The same reaction mechanism is assumed (eq 7).


(6)


(7)

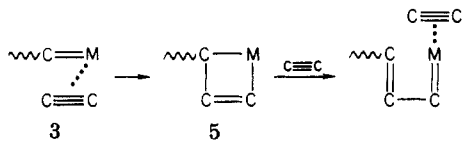
For the following reasons, it is inferred that metal carbenes mediate the Mo- and W-catalyzed polymerization of acetylenes as well as olefin metathesis: (i) identical catalysts (e.g., WCl_6·Ph_4Sn,[7,27] $W(CO)_6$–CCl_4–$h\nu$[9,10]) effect both olefin metathesis (including metathesis polymerization) and polymerization of acetylenes, (ii) isolated metal carbenes [$Ph(CH_3O)C{=}W(CO)_5$ and $Ph_2C{=}W(CO)_5$] can induce not only olefin metathesis[28] but also polymerization of acetylenes,[29] and

Scheme I



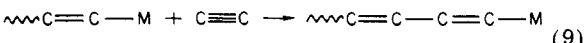
(iii) the presence of tungsten dichlorocarbene in the $W(CO)_6$–CCl_4–$h\nu$ system has been proved by the trapping method.[30] It is possible and interesting to regard acetylenes as extreme members of cycloolefins, that is, two-membered rings in which the carbon chain connecting the two sp^2 carbons is replaced with a carbon–carbon single bond.

According to the discussion above, the following propagation reaction involving metal carbenes (**3**) and metallacyclobutenes (**5**) can be depicted for the present polymerization:



(8)

We proposed this mechanism on the basis of the analogy between polymerization of acetylenes and olefin metathesis.[6] Katz and Lee later supported it by polymerizing acetylenes with isolated metal carbenes.[29] If the metal–carbene mechanism is valid, then the propagation process involves cleavage of both π-bonds of the acetylenic monomer, and therefore the polymer structure should, in a strict sence, be expressed by $=(C{-}C{=})_n$ and not by $-(C{=}C{-})_n$. On the other hand, insertion of the monomer to alkenylmetals (**6**), that is, simple opening of one π-bond of the monomer, has been postulated as propagation reaction in the acetylene polymerization by Ziegler catalysts (eq 9).[31] Thus there



(9)

are still many ambiguous aspects to be solved about polymerization mechanism.

Features of Mo- and W-Based Catalysts and Polymers Formed Therewith

Scheme I compares Mo- and W-based catalysts with Ziegler catalysts and polymers from sterically hindered acetylenes with polyacetylene.

The Mo and W catalysts exploited by us are classified as follows: (i) $MoCl_5$, WCl_6, (ii) $MoCl_5$·Ph_4Sn, WCl_6·

(22) (a) Masuda, T.; Okano, Y.; Kuwane, Y.; Higashimura, T. *Polym. J.* **1980**, *12*, 907. (b) Okano, Y.; Masuda, T.; Higashimura, T. *Ibid.* **1982**, *14*, 477.
(23) Higashimura, T.; Deng Y.-X.; Masuda, T. *Macromolecules* **1982**, *15*, 234.
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Ph_4Sn, and (iii) $Mo(Co)_6$–CCl_4–*hν*, $W(CO)_6$–CCl_4–*hν*. The first group is active enough toward monosubstituted acetylenes. Trace amounts of water and alcohols accelerate the polymerization;[5,12] these may be essential for the formation of "a spectator oxo group".[32] Catalysts of the second type polymerize not only monosubstituted but disubstituted acetylenes as well. Organometallics other than Ph_4Sn such as *n*-Bu_4Sn, Et_3SiH, and Ph_4Bi are also useful as cocatalysts.[16b] These cocatalysts are considered to alkylate and reduce the transition metals to form active catalyst sites. The third type of catalysts yield high polymers, though most disubstituted acetylenes cannot be polymerized and the solvent is usually restricted to carbon tetrachloride. A tendency is observed as to the difference between Mo and W catalysts: Acetylenes having electron-withdrawing groups (1-chloro-2-phenylacetylene[16] and propiolic acid[33]) are polymerized solely by Mo catalysts while those with electron-donating groups ((trimethylsilyl)acetylene[34] and ethoxyacetylene[35]) only by W catalysts.

When comparison is made with Ziegler catalysts, one of the most important characteristics of Mo and W catalysts is that they can produce high polymers from sterically hindered acetylenes such as *tert*-butylacetylene and several disubstituted acetylenes. These catalysts, however, do not appear to be very active for the unsubstituted acetylene.[36] Consequently it is concluded that Mo and W catalysts are especially useful for the polymerization of sterically hindered acetylenes, wheras Ziegler catalysts like $Ti(O\text{-}n\text{-}Bu)_4$·$4Et_3Al$ are useful for acetylene polymerization. Another interesting point is that Mo and W catalysts can polymerize some heteroatom-containing acetylenes (e.g., propiolic acid[33] and propargyl alcohol[37]) toward which Ziegler catalysts are inactive.

As seen in Scheme I, the polymers from *tert*-butylacetylene and several disubstituted acetylenes strikingly differ in property from polyacetylene. These unique properties originate from the presence of substituent(s) and the main chains being out of plane thereby. Among the properties, high oxidative stability and high solubility are two important ones that polyacetylene does not possess. The high stability is due to that unpaired electrons, which will cause polymer oxidation and degradation, do not exist on the main chain. These polymers dissolve completely in organic solvents such as toluene, and tough films can readily be prepared by casting polymer solution.

Reactions and Applications of Polymers

Reactions of the polymers from substituted acetylenes can afford new polymers. Eq 10[38] and 11[34] demonstrate that the main chain of such polymers is reactive enough, leading new polymers (conversions do not necessarily reach 100%). Acetylenic polymers with hydrophilic groups are rather difficult to prepare directly by the polymerization using Mo and W catalysts but can be obtained by reactions of side group(s) of polymers (e.g., eq 12[39]).

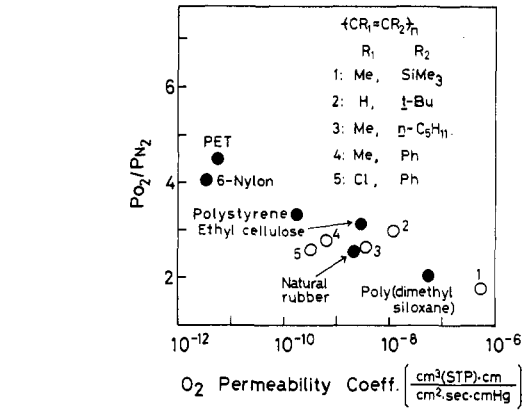
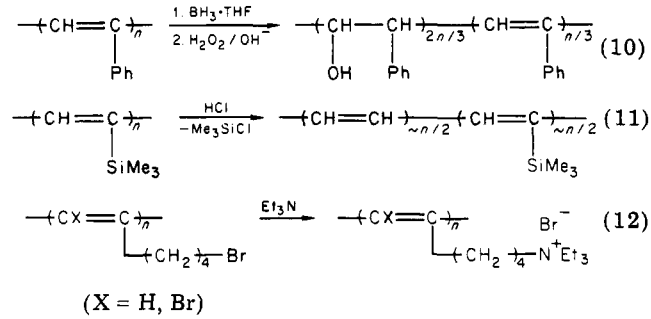
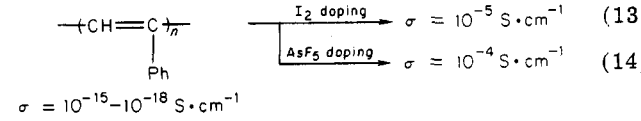


Figure 2. Gas permeability and selectivity of typical polymers and those from substituted acetylenes (25 °C).



Polymer degradation is a reaction in which the main change is molecular weight decrease. Among the film-forming polymers in our work, poly(2-alkynes) readily undergoes degradation ($\bar{M}_w$: from 10^5 to 10^3) upon irradiation with γ-rays in air to become soluble in polar solvents like acetone.[40] Resists, which are defined as film-forming materials whose solubilities change by irradiation with UV light, electron beams, or X-rays, play an important role in the manufacture of large-scale integrated circuits.[41] It may be possible to utilize our polymes as "positive-working" resists.

Though most polymers of substituted acetylenes are electrical insulators, doping with appropriate electron acceptors enhances their conductivity (e.g., eq 13[42] and 14[43]). Since the conductivity of poly(phenylacetylene)



appreciably increases even in the presence of certain gases (CO, CO_2, SO_2, etc.), it has been investigated whether the polymer can apply to a low-cost early-

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warning fire-detection system.[44] Poly(phenylacetylene) absorbs lights of long wavelength to exhibit a photoconductive property.[45]

Membranes for oxygen enrichment have recently been the subject of intensive research.[46] Poly(dimethylsiloxane) is famous for its highest permeability coefficient [P; $cm^3(STP)\cdot cm/(cm^2\cdot s\cdot cmHg)$] to oxygen among those of the polymers so far examined ($P_{O_2} = 6.0 \times 10^{-8}$; $P_{O_2}/P_{N_2} = 1.9$). We found that some of the present polymers exhibited fairly high permeabilities[47,48] (see Figure 2). Quite interestingly, poly[1-(trimethylsilyl)-1-propyne], which was prepared with halides of niobium (Nb) and tantalum (Ta) as catalysts, showed a value about 10 times larger than that of poly(dimethylsiloxane) ($P_{O_2} = (61 \times 10^{-8})-(83 \times 10^{-8})$; $P_{O_2}/P_{N_2} = 1.7$).[48] The high gas permeability of poly(dimethylsiloxane) has been attributed mainly to the large free volume resulting from the flexible backbone. Findings with the present polymers must be explained in other terms since the polymers are considerably rigid.

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Concluding Remarks

In this account the effectiveness of Mo- and W-based catalysts for the polymerization of substituted acetylenes has been examined. We claim that the present polymerization is, following olefin metathesis and metathesis polymerization, the third important reaction mediated by W and Mo carbenes.

Recently it has been found that disubstituted acetylenes are polymerized by organo-Nb(III) and -Ta(III)[49] and by halides of Nb(V) and Ta(V).[48,50] It is worth noting that the latter catalysts afford poly(1-phenyl-1-propyne)[50] and poly[1-(trimethylsilyl)-1-propyne][48] whose molecular weights reach about one million. It is reported that acetylenes are polymerized by lanthanide-containing catalysts as well.[51] Thus the study on the polymerization of acetylenes will further advance, promoted by the exploitation of novel catalysts.

Only a few studies have been performed on the application of polymers from substituted acetylenes. We expect that useful functions will be developed.

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Thermal Ring-Opening Cycloadditions of Cyclopropyl Derivatives with Activated Olefins

TAKASHI TSUJI* and SHINYA NISHIDA*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060, Japan

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Cyclopropane is conspicuous among alicyclic compounds by its similarity to olefins in its physical and chemical properties.[1] Thus, three-membered carbocycles are known to effectively conjugate with unsaturated groups, are susceptible to attack by electrophiles, and are capable of undergoing nucleophilic ring opening when the ring is activated with strongly electron-withdrawing groups.[1,2] In addition, the lability of cyclopropanes to homolytic ring cleavages[1] and the high ability of cyclopropyl groups to stabilize adjacent electron-deficient centers[3] have been well-documented. These multifaceted features confer various interesting aspects on the chemistry of cyclopropyl derivatives. Among such reactions that are characteristic to cyclopropyl derivatives, ring-opening cycloadditions with unsaturated compounds are of particular interest, since odd-membered ring compounds can be prepared from two fragments in a single operation.

In the structural and geometrical isomerizations of cyclopropanes, trimethylene biradicals are commonly

Takashi Tsuji was born in Osaka, Japan, in 1939 and received his B.E. and his Ph.D. from Osaka University. He joined the faculty of Osaka University in 1967 and moved to Hokkaido University in 1971, where he is currently Associate Professor of Chemistry. From 1968 to 1970, he was a postdoctral research fellow with Edward M. Kosower at the State University of New York at Stony Brook. His research interests include the chemistry of strained polycyclic compounds, especially molecules of novel π-electron systems.

Shinya Nishida was born in Osaka, Japan, in 1931 and received his B.S. and Ph.D. from Osaka University. After postdoctoral works with Herbert C. Brown at Purdue University and with Derek H. R. Barton at Imperial College of Science and Technology, he joined the faculty of Osaka University in 1962 and moved to Hokkaido University in 1970, where he is presently Professor of Chemistry. His major research interests are in the chemistry of small ring compounds and mechanistic studies on organic reactions.

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