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Polymerization of 1-Chloro-2-phenylacetylene by $MoCl_5$-Based Catalysts[1]

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ABSTRACT: Polymerization of 1-chloro-2-phenylacetylene catalyzed by mixtures of $MoCl_5$ with various organometallics of main-group metals provided in high yields a polymer having weight-average molecular weights of 1×10^5–12×10^5. n-Bu_4Sn, Et_3Si, and Ph_3Bi were especially effective among the organometallic cocatalysts examined. Aromatic and halogenated hydrocarbons worked as useful polymerization solvents. The polymer formed was a light yellow soluble solid. On the other hand, 1-chloro-2-phenylacetylene gave mainly a methanol-soluble oligomer in the presence of $MoCl_5$ alone. It was inferred that the polymerization and the oligomerization proceed via a metal carbene and an alkynylmetal, respectively.

In a previous paper we have reported that 1-chloro-2-phenylacetylene is polymerized by a catalyst formed by UV irradiation of $Mo(CO)_6$ in carbon tetrachloride.[3] Since in this polymerization both UV irradiation and carbon tetrachloride are indispensable to the formation of the active species, we designated the catalyst system $Mo(CO)_6$–CCl_4–$h\nu$. It is of great interest that $Mo(CO)_6$–CCl_4–$h\nu$ yields poly(1-chloro-2-phenylacetylene) having a weight-average molecular weight ($\bar{M}_w$) up to two million.

$MoCl_5$ alone is capable of polymerizing monosubstituted acetylenes such as phenylacetylene[4] and *tert*-butylacetylene.[5] Mixtures of $MoCl_5$ with organotins (e.g., Ph_4Sn and n-Bu_4Sn) can polymerize not only monosubstituted but also disubstituted acetylenes like 2-alkynes.[6] 1-Chloro-2-phenylacetylene is a disubstituted acetylene having an electron-withdrawing chlorine adjacent to the C≡C bond. It appears interesting to examine whether transition-metal chlorides, such as $MoCl_5$, alone are active and what are effective organometalic cocatalysts. A characteristic of $MoCl_5$-based catalysts as compared with the $Mo(CO)_6$–CCl_4–$h\nu$ system is that by selecting cocatalysts and solvents it is possible to control the polymerization rate and the molecular weight.

This paper deals with the polymerization of 1-chloro-2-phenylacetylene catalyzed by mixtures of $MoCl_5$ with various organometallics of main-group metals. It has been revealed that while $MoCl_5$ alone yields mainly an oligomeric mixture, $MoCl_5$ in conjunction with organotins, -silicons, and -bismuth give a polymer having $\bar{M}_w$ of 1×10^5–12×10^5 in high yields.

Experimental Section

1-Chloro-2-phenylacetylene was offered by Sanyo Chemical Industries Ltd., Japan. Transition-metal chlorides and organometallics were commercially obtained and usually employed without further purification.

The catalysts comprising two components were usually prepared by mixing them at a 1:1 molar ratio in solution and subsequently aging the mixtures at 30 °C for 15 min. Unless otherwise specified, polymerizations were carried out under nitrogen in toluene at $[M]_0 = 1.0$ M, [Cat] = [Cocat] = 20 mM, 30 °C for 24 h.

Monomer conversions (consumptions) were determined by gas chromatography (poly(ethylene glycol) 6000, 3 m; 135 °C; bromobenzene as internal standard). Polymers were isolated by the precipitation of reaction mixtures into a large amount of methanol. Methanol-soluble oligomeric mixtures were isolated by evaporating the methanol, dissolved in toluene, washed with dilute hydrochloric acid and water, and again isolated by evaporating the toluene. The yields of polymers and oligomeric mixtures were determined by gravimetry.

Molecular weights of polymers were calculated from their intrinsic viscosities (in toluene, 30 °C) by use of the following equation obtained in a previous paper:[3]

$$[\eta] = K\bar{M}_w{}^a \quad (K = 10^{-6.06}\ \mathrm{dL/g}; \quad a = 1.07)$$

Table I
Attempted Polymerization of 1-Chloro-2-phenylacetylene by Group 4-7 Transition-Metal Chlorides[a]

catalyst	conversion, %	polymer yield,[b] %
$TiCl_4$	0	0
$ZnCl_4$	0	0
VCl_4	14	0
$NbCl_5$	0	0
$TaCl_5$	23	3
$MoCl_5$	57	5
WCl_6	0	0
$ReCl_5$	33	0

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 1.0$ M, [Cat] = 20 mM. [b] Methanol-insoluble part.

For comparison, some molecular weights were determined directly by the light-scattering method with a Chromatix KMX-6 photometer. The values obtained for the same sample by both methods agreed fairly well (see Tables II and III). Molecular weight distributions (MWD) of oligomers were measured in chloroform solution (1% (w/v)) with a Jasco Triroter II chromatograph.

Results

Attempted Polymerization by Transition-Metal Chlorides. At first we examined whether transition-metal chlorides alone can catalyze the polymerization of 1-chloro-2-phenylacetylene. The reaction was carried out in toluene at 30 °C for 24 h. As shown in Table I, 1-chloro-2-phenylacetylene reacted in the presence of VCl_4, $TaCl_5$, $MoCl_5$, or $ReCl_5$ among several group 4-7 transition-metal chlorides; $MoCl_5$ was the most active. The principal product, however, was a methanol-soluble oligomeric mixture. Using the most active $MoCl_5$, we then investigated the effect of organometallics of main-group metals as cocatalysts.

Cocatalyst Effect on the Polymerization by $MoCl_5$. Table II shows results for the polymerization by $MoCl_5$ in the presence of organotin cocatalysts. The reaction was carried out under the same conditions as in the case of transition-metal chlorides alone. When Me_4Sn and n-Bu_4Sn were used as cocatalysts, the reaction proceeded quantitatively to give mainly polymers having very high molecular weights ($\bar{M}_w = 7 \times 10^5$–$8 \times 10^5$). Thus the tetraalkyltins are excellent cocatalysts to polymerize 1-chloro-2-phenylacetylene by $MoCl_5$. n-Bu_4Sn (bp 145 °C (10 mm)) is less volatile and hence easier to handle than Me_4Sn (bp 78 °C). Though not as effective as the tetraalkyltins, Ph_4Sn also yields a considerable amount of methanol-insoluble polymer. On the other hand, the polymerization in the presence of organotin chlorides (n-Bu_3SnCl, n-Bu_2SnCl_2, n-$BuSnCl_3$, and Ph_3SnCl) gave large amounts of methanol-soluble oligomers, indicating that

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Table II
Effect of Organotin Cocatalysts on the Polymerization of 1-Chloro-2-phenylacetylene by $MoCl_5$[a]

cocatalyst	conversion, %	polymer[b] yield, %	$\overline{M}_w/10^4$
Me_4Sn	100	89	77
n-Bu_4Sn	100	91	69
Ph_4Sn	89	45	39[c]
n-Bu_3SnCl	46	12	
n-Bu_2SnCl_2	85	2	
n-$BuSnCl_3$	75	2	
Ph_3SnCl	68	13	

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 1.0$ M, [Cat] = [Cocat] = 20 mM. [b] Methanol-insoluble part. [c] 48×10^4 by the light-scattering method.

Table III
Effect of Organosilicon Cocatalysts on the Polymerization of 1-Chloro-2-phenylacetylene by $MoCl_5$[a]

cocatalyst	conversion, %	polymer[b] yield, %	$\overline{M}_w/10^4$
Et_3SiH	100	75	64[c]
$PhMe_2SiH$	100	91	122[d]
$(Me_3Si)_2O$	100	85	28
Me_3SiOn-Bu	95	70	14[e]
$PhMe_3Si$	85	19	
$PhEt_3Si$	78	11	
Me_3SiCl	83	6	
Ph_2SiCl_2	80	4	

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 1.0$ M, [Cat] = [Cocat] = 20 mM. [b] Methanol-insoluble part. [c] 82×10^4 by the light-scattering method. [d] 104×10^4 by the light-scattering method. [e] 15×10^4 by the light-scattering method.

Table IV
Effect of Ph_3X (X = Group 5B Elements) as Cocatalysts on the Polymerization of 1-Chloro-2-phenylacetylene by $MoCl_5$[a]

cocatalyst	conversion, %	polymer[b] yield, %	$\overline{M}_w/10^4$
Ph_3N	0	0	
Ph_3P	0	0	
Ph_3As	0	0	
Ph_3Sb	67	46	83
Ph_3Bi	96	83	88

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 1.0$ M, [Cat] = [Cocat] = 20 mM. [b] Methanol-insoluble part.

they hardly work as cocatalysts.

The organosilicon cocatalysts used are classified into four types according to the bonds in which silicon is participating: (a) Si–H, (b) Si–O, (c) Si–C only, and (d) Si–Cl. Among them, compounds of types a and b were effective cocatalysts, whereas those of types c and d were not (Table III). Hydrosilanes (type a) tended to achieve high molecular weights, while silanes bearing the Si–O bond(s) (type b) gave polymers having relatively low molecular weights; thus the molecular weights range from ca. 1×10^5 to 12×10^5.

Table IV shows the effect of triphenyl-substituted compounds of group 5 main-group elements. Only Ph_3Sb and Ph_3Bi, which are weak Lewis bases, effected polymerization; the latter was an especially useful cocatalysts. The more basic Ph_3N, Ph_3P, and Ph_3A seem to form complexes with $MoCl_5$ and thereby inactivate it.

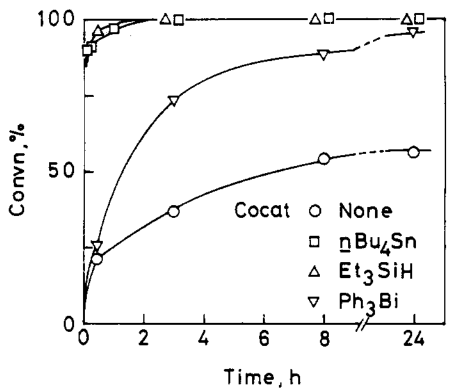


Figure 1. Time courses for the polymerizations of 1-chloro-2-phenylacetylene by $MoCl_5$-based catalysts (in toluene, 30 °C, $[M]_0 = 1.0$ M, [Cat] = 20 mM, [Cocat] = 0 or 20 mM).

Table V
Polymerization of 1-Chloro-2-phenylacetylene by $MoCl_5$-n-Bu_4Sn (1:1) in Various Solvents[a]

solvent	conversion, %	polymer[b] yield, %	$\overline{M}_w/10^4$
benzene	100	90	74
toluene	100	91	69
cyclohexane	61	61	49
CCl_4	88	86	85
PhCl	100	82	66
$(CH_2Cl)_2$	100	87	46
anisole	54	52	46
$PhCO_2CH_3$	25	2	
$PhCOCH_3$	0	0	

[a] Polymerized at 30 °C for 24 h; $[M]_0 = 1.0$ M, $[MoCl_5$-n-$Bu_4Sn]$ = 20 mM. [b] Methanol-insoluble part.

Though the cocatalytic activities of organoaluminums (Et_3Al, Et_2AlCl, and $EtAlCl_2$) and metal hydrides ($LiAlH_4$, $NaBH_4$, and NaH) were also examined, methanol-insoluble poly(1-chloro-2-phenylacetylene) was hardly obtained with them.

The conversion of 1-chloro-2-phenylacetylene in the presence of n-Bu_4Sn, Et_3SiH, and Ph_3Bi as cocatalysts was faster than in the presence of $MoCl_5$ alone (Figure 1). Especially, when the former two cocatalysts were used the conversions of the monomer reached about 90% in 5 min. Thus organometallic cocatalysts remarkably affect not only the molecular weight of the product but also the reaction rate.

Polymerization by $MoCl_5$–n-Bu_4Sn under Various Conditions. As has been clarified above, an equimolar mixture of $MoCl_5$ with n-Bu_4Sn ($MoCl_5$–n-Bu_4Sn) is one of the most effective $MoCl_5$-based catalysts for 1-chloro-2-phenylacetylene polymerization. Therefore, the effect of reaction conditions was investigated with $MoCl_5$–n-Bu_4Sn as catalyst system.

High polymer yields and molecular weights were generally achieved in aromatic and halogenated hydrocarbons as polymerization solvents (Table V). Aliphatic hydrocarbons are not very preferable because they are poor solvents for both the catalyst and the polymer. As to oxygen-containing solvents, both conversion and polymer yield decreased markedly in the order of anisole, methyl benzoate, and acetophenone, that is, with increasing polarity.

The effects of temperature, cocatalyst-to-catalyst ratio, and catalyst aging time are shown in Table VI. The

Table VI

Effects of Temperature, Cocatalyst-to-Catalyst Ratio, and Catalyst Aging Time on the Polymerization of 1-Chloro-2-phenylacetylene by $MoCl_5$-n-Bu_4Sn[a]

temp, °C	$[n\text{-}Bu_4Sn]/[MoCl_5]$	aging time, min	conversion, %	polymer[b] yield, %	polymer[b] $\bar{M}_w/10^4$
30	1.0	15	100	91	69
0	1.0	15	100	97	81
80	1.0	15	100	86	46
120[c]	1.0	15	100	13	
30	0.25	15	82	3	
30	0.5	15	93	84	68
30	2.0	15	100	94	63
30	4.0	15	95	92	61
30	1.0	0	82	49	59
30	1.0	5	66	54	49
30	1.0	60	100	95	80
30	1.0	180	100	100	95

[a] Polymerized in toluene for 24 h; $[M]_0$ = 1.0 M, $[MoCl_5]$ = 20 mM. [b] Methanol-insoluble part. [c] Polymerized for 6 h in xylene.

polymer yield was high at polymerization temperatures between 0 and 80 °C, and was appreciably lower at 120 °C. The lower the polymerization temperature, the higher the polymer molecular weight. The cocatalyst-to-catalyst ratio hardly affected the yield and molecular weight of the polymer as long as it was maintained within one to four. the 1:1 catalyst must be aged for about 15 min or longer to be effective enough. thus, the reaction conditions for the run of the first row in Table VI are typical ones to obtain high molecular weight polymer in high yield.

Attempted Polymerization by WCl_6-Based Catalysts. Hydrocarbon acetylenes (phenylacetylene,[4] *tert*-butylacetylene,[5] and 2-alkynes[6]) are polymerized not only by $MoCl_5$-based catalysts but also by the WCl_6-based counterparts. Therefore, we examined the catalytic activities of mixtures of WCl_6 with a few organometallics (reaction conditions are the same as in Table II). The results are as follow: (cocatalysts, conversion %, polymer yield %) n-Bu_4Sn, 32, 19; Et_3SiH, 24, 0; Ph_3Bi, 16, 12. Thus WCl_6-based catalysts are hardly active. This corresponds to the fact that $Mo(CO)_6$–CCl_4–$h\nu$ can polymerize 1-chloro-2-phenylacetylene, whereas $W(CO)_6$–CCl_4–$h\nu$ cannot.[3] The presence of chlorine adjacent to the C≡C bond in the monomer should be the cause for such a high selectivity with respect to catalyst metal.

Structure and Properties of the Polymer. Anal. Calcd for $(C_8H_5Cl)_n$: C, 70.35; H, 3.69; Cl, 25.96. Found: C, 70.64; H, 3.86; Cl, 25.70; O, 0.00. IR 1650–1550 (w, conjugated C=C), 820 (m, =C—Cl) cm^{-1}. Thus the polymer formed is considered to have the expected structure 1.

$$-\!\left[\text{CCl}{=}\text{CPh}\right]\!_n\!-$$

1

Poly(1-chloro-2-phenylacetylene) obtained with $MoCl_5$-based catalysts is a light yellow air-stable solid; it is soluble in such solvents as toluene, carbon tetrachloride, and tetrahydrofuran, and a tough film can be prepared by solution casting. This polymer was an insulator ($\sigma < 10^{-18}$ S cm^{-1}, and not paramagnetic ($<10^{15}$ spin/g). These properties do not substantially differ from those of poly(1-chloro-2-phenylacetylene) formed with $Mo(CO)_6$–CCl_4–$h\nu$.[3]

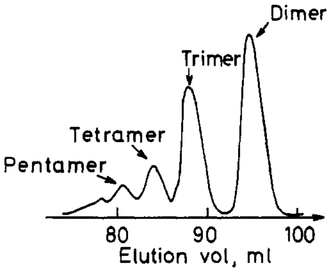
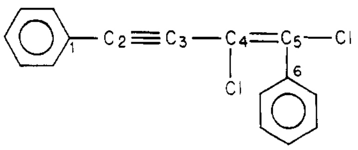


Figure 2. Liquid chromatogram of the oligomeric mixture of 1-chloro-2-phenylacetylene (sample from Table I, $MoCl_5$ system).

Oligomerization of 1-Chloro-2-phenylacetylene. As described above, the reaction of 1-chloro-2-phenylacetylene by $MoCl_5$ in toluene gave mainly a methanol-soluble oligomeric mixture (yield 52%; see Table I). The oligomerization occurred similarly in some other solvents (reaction conditions are the same as in Table I): (solvent, conversion %, oligomer yield %) 1,2-dichloroethane, 60, 55; anisole, 38, 31.

The oligomeric mixture formed consisted of dimer through hexamer (Figure 2). The dimer, fractionated by liquid chromatography, was a light yellow liquid. Its molecular weight was 279 (theoretical value 273) according to vapor pressure osmometry, and the analytical data were as follows. Anal. Calcd for $(C_8H_5Cl)_2$: C, 70.35; H, 3.69; Cl, 25.96. Found: C, 69.98; H, 4.02; Cl, 25.27. In the IR spectrum of the dimer, bands were observed at 2200 (C≡C), 810, and 735 (both =C—Cl) cm^{-1}, but the band at 650 cm^{-1} (≡C—Cl) seen in the spectrum of the monomer was absent. From these and the following ^{13}C NMR data (assigned by the additivity rule[7]), dimer structure 2 is most probable:



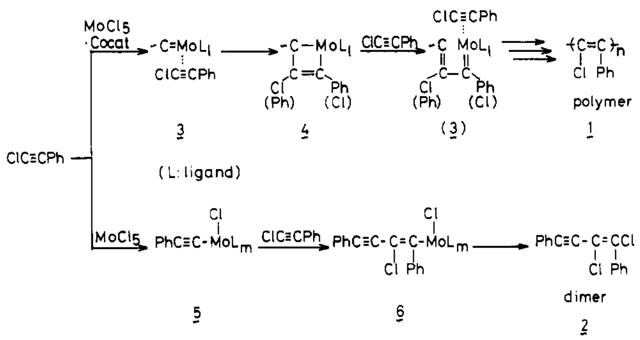
2

^{13}C NMR ($CDCl_3$) δ 135.49 (C_6, s), 131.63 (C_5, s), 129.60–127.86 (others), 121.58 (C_1, s), 110.05 (C_4, s), 97.57 (C_3, s), 85.04 (C_2, s).

Discussion

The present study has revealed that the reaction of 1-chloro-2-phenylacetylene by $MoCl_5$-based catalysts affords a wide spectrum of products from dimer to high molecular weight polymer. It is unlikely that the polymer and oligomers have been formed simultaneously via an identical active species. We consider the mechanisms

Scheme I



shown in Scheme I reasonable.

The polymerization process should involve a Mo carbene as active species: Mixtures of either WCl_6 or $MoCl_5$ with organometallics metathesize olefins[8] and polymerize cycloolefins.[9] A mechanism involving metal carbenes, which was proposed by Hérisson and Chauvin,[10] is now generally accepted. In this analogy, in the presence of an organometallic cocatalyst and 1-chloro-2-phenylacetylene, $MoCl_5$ might be converted to monomer-coordinated Mo carbene **3**. The propagation reaction proceeds via **3** and molybdacyclobutene **4** as shown in Scheme I.[11,12]

The following dimerization mechanism seems probable: Elimination of chlorines from $MoCl_5$ by 1-chloro-2-phenylacetylene will yield a reduced Mo complex.[13] Alkynylmolybdenum **5** is formed by oxidative addition of the acetylene to the Mo complex. Then the acetylene is inserted in **5** to give alkenylmolybdenum **6**; the subsequent reductive elimination leads to dimer. If a few molecules of the acetylene are repeatedly inserted in **5**, trimer or a higher oligomer will be produced. However, the formation of a high polymer via **5**, **6**, etc. is unlikely since these species easily undergo reductive elimination. A similar mechanism has been proposed for the dimerization of monosubstituted α-hydroxyacetylenes by the Wilkinson catalyst.[14]

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Registry No. 2, 88180-42-1; poly(1-chloro-2-phenylacetylene), 81953-16-4; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; Me_4Sn, 594-27-4; Bu_4Sn, 1461-25-2; Ph_4Sn, 595-90-4; Bu_3SnCl, 1461-22-9; Bu_2SnCl_2, 683-18-1; $BuSnCl_3$, 1118-46-3; Ph_3SnCl, 639-58-7; Et_3SiH, 617-86-7; $PhMe_2SiH$, 766-77-8; $(Me_3Si)_2O$, 107-46-0; Me_3SiOBu, 1825-65-6; $PhMe_3Si$, 768-32-1; $PhEt_3Si$, 2987-77-1; Me_3SiCl, 75-77-4; Ph_2SiCl_2, 80-10-4; Ph_3Sb, 603-36-1; Ph_3Bi, 603-33-8.

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Liquid Crystal Block Copolyesters. 3. Isomerization Polymerization of Block Copolyesters Containing Cyclohexane and Benzene Rings

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ABSTRACT: Attempts to synthesize poly(oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl) (VII) and poly[oxy-*cis*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (XI) led to the preparation of poly[oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy-1,4-phenyleneoxyterephthaloyl] (I) and poly[oxy(*cis,trans*)-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (II), respectively. Poly[oxy-*trans*-1,4-cyclohexyleneoxycarbonyl-*trans*-1,4-cyclohexylenecarbonyl-*b*-oxy(2-methyl-1,3-phenylene)oxyterephthaloyl] (X) was synthesized and shown to form mesomorphic solutions.

Introduction

This is the third in a series of papers that describe the synthesis and characterization of a number of block copolyesters which contain cyclohexane and benzene rings. A number of these block copolyesters in solution have been shown to rotate the plane of polarized light; e.g., they form birefringent fluid phases.

The second paper in the series described the synthesis and characterization of among other block copolyesters, what we reported as poly(oxy-*cis*-1,4-cyclohexyleneoxy-