Articles

Transition Metal Carbonyl Catalysts for Polymerizations of Substituted Acetylenes

**Kaitian Xu, Han Peng, Jacky Wing Yip Lam, Tommy Wan Hong Poon,
Yuping Dong, Hongyao Xu, Qunhui Sun, Kevin Ka Leung Cheuk, Fouad Salhi,
Priscilla Pui Sze Lee, and Ben Zhong Tang***

*Department of Chemistry, Hong Kong University of Science & Technology,
Clear Water Bay, Hong Kong, China*

Received May 16, 2000; Revised Manuscript Received July 18, 2000

ABSTRACT: Most of the existing metal carbonyl catalysts for acetylene polymerizations need to be preactivated by chlorine-containing additives or by UV irradiation in halogenated solvents. In this work, we developed a series of “simple” metal carbonyl catalysts of general structure $M(CO)_xL_y$ (M = Mo, W), none of which require additives or pre-photoirradiation, most of which are air- and moisture-stable, and some of which work well in nonhalogenated solvents. The acetonitrile complexes $M(CO)_3(NCCH_3)_3$ initiated polymerizations of a variety of mono- and disubstituted acetylenes at room temperature. The arene and diene complexes $W(CO)_3$(mes) and $Mo(CO)_3$(nbd) (mes = mesitylene, nbd = 2,5-norbornadiene) are tolerant of polar groups and effected polymerizations of functional acetylenes containing ester, ether, and cyano groups. The halogenated complexes $MI_2(CO)_3(NCCH_3)_2$ catalyzed polymerizations of phenylacetylene in toluene. The chlorine-containing acetylene monomers $ClC{\equiv}CC_6H_5$ and $ClC{\equiv}CC_6H_{13}$ were readily polymerized by the Mo complexes in nonhalogenated solvents such as toluene and dioxane, giving polymers with high molecular weights (M_w up to 883 × 10^3) in high yields (up to 100%).

Introduction

Studies on conjugated polymers are one of the most active research areas in contemporary macromolecule science.[1] Polyacetylene, whose doped form exhibits metallic conductivity, is an archetypal conjugated polymer. Polyacetylenes with suitable substituents (substituted polyacetylenes) have been found to possess not only superior stability and tractability but also interesting materials properties such as photoconductivity, solvatochromism, optical nonlinearity, light emissivity, optical activity (helical chirality), liquid crystallinity, magnetic susceptibility, and self-organizability.[2,3] It is envisioned that substituted polyacetylenes may find innovative high-technology applications, and it is thus of interest to develop versatile polymerization systems for the synthesis of the polymers.

Exploration of new catalysts plays a vital role in the development of new polymerization systems. Many inorganic compounds and organometallic complexes have been found to effect acetylene polymerization,[4] among which the halides of molybdenum and tungsten, i.e., $MoCl_5$ and WCl_6, are most widely used. These metal halides are, however, extremely air- and moisture-sensitive and must be handled in dry and inert atmosphere. The shipping and storage of these catalysts require extraordinary care, and the air and moisture in the polymerization reactors must be rigorously excluded. One obvious consequence of such procedures is the incurrence of high production cost, and industrial manufacturers would particularly welcome those catalysts that are environmentally stable and easy to handle.

Molybdenum and tungsten hexacarbonyls [$M(CO)_6$; M = Mo, W] are air- and moisture-stable, but the complexes themselves are sluggish catalysts for acetylene polymerization.[4] Irradiation by UV light can convert the metal carbonyls into active catalytic species,[5] but industrial production lines seldom utilize photochemical processes. Noticing that $M(CO)_6$ can readily undergo many chemical reactions,[6] in 1989 we prepared a few “simple” complexes of general structure $M(CO)_xL_y$ with the aim of activating the metal carbonyls by organic ligands (L).[7] We succeeded in developing two groups of new catalysts from such complexes and found that $M(CO)_3(NCCH_3)_3$ and $M(CO)_3$(mes) (mes = mesitylene) effectively initiated polymerizations of acetylenes with alkyl and aryl substituents in carbon tetrachloride (CCl_4) without photoirradiation (yield up to 85%, M_w up to 1.1 × 10^6).[7] Other research groups have also developed some metal−carbonyl catalysts of similar structures, most of which have been found to work in halogenated solvents (e.g., CCl_4) or in the presence of chlorine-containing additives (e.g., chloronil, Lewis acids).[8,9] Organometallic complexes are generally sensitive to polar functional groups, and almost all the monomers polymerized by the metal carbonyl catalysts so far are acetylenes with nonpolar substituents. It is of academic interest and practical value to check whether the metal

---

* Corresponding author. E-mail: tangbenz@ust.hk.

10.1021/ma000843a CCC: $19.00

carbonyl complexes can initiate polymerizations of functional acetylenes with polar moieties.

In this work, we extended our efforts in developing metal carbonyl-based catalysts for acetylene polymerizations. We systematically studied catalytic behaviors of a series of $M(CO)_xL_y$ complexes in the polymerizations of different kinds of acetylene monomers. We found that some of the metal complexes were tolerant of polar groups and could polymerize alkynes with different functional substituents. When we incorporated halogen atoms into the molecular structures of the metal−carbonyl complexes and the acetylene monomers, the polymerization reactions readily proceeded in nonhalogenated solvents.

Experimental Section

Materials. Except for the $M(CO)_3(NCCH_3)_3$ and $MI_2(CO)_3(NCCH_3)_2$ complexes, all the other complexes of molybdenum and tungsten carbonyls used in this study were purchased from Aldrich and were used as received without further purification. The $M(CO)_3(NCCH_3)_3$ complexes were prepared according to published procedure,[7,10] while the $MI_2(CO)_3(NCCH_3)_2$ complexes were prepared using Baker's method[11] with some modifications. A typical example of experimental procedure for the preparation of $MoI_2(CO)_3(NCCH_3)_2$ is given below.

A suspension of 0.160 g (0.61 mmol) of $Mo(CO)_6$ in vigorously degassed acetonitrile was refluxed under argon for 24 h. The homogeneous solution obtained was cooled to 0 °C, followed by the addition of 0.155 g (0.61 mmol) of I_2, resulting in the immediate formation of a red-brown solution. Removal of the solvent under reduced pressure gave a brown crystalline complex in quantitative yield. IR (KBr) ν (cm^{-1}): 2040, 1970 ($C{=}O$), 2358, 2320 ($N{\equiv}C$). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 2.4 (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 226.0 ($C{=}O$), 118.0 ($N{\equiv}C$), 4.1 (CH_3).

Toluene (Lab-Scan) and dioxane (Aldrich) were dried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl prior to use. Carbon tetrachloride (Lab-Scan) was distilled over calcium hydride. Propargyl chloride, 2-decyne, phenylacetylene, 1-phenyl-1-butyne, and 1-octyne were purchased from Farchan, distilled from calcium hydride, and stored in a dark, cold place. The synthesis and characterization of the acetylene monomers containing a silicon stereogenic center (cf. Table 1, no. 5) and polar functional groups (cf. Table 4) were reported elsewhere.[3,7,12] All the other acetylene monomers were prepared according to literature methods.[4,13] Other solvents and reagents were all Aldrich products of high purity and were used as received. A typical experimental procedure for the preparation of 1-chloro-1-octyne monomer is given below.

Into a two-necked 500 mL round-bottomed flask equipped with a nitrogen inlet, a pressure-equalized dropping funnel, and a magnetic stirrer were placed 60 mL of anhydrous THF and 14.8 mL (0.1 mol) of 1-octyne. To this solution was added 67 mL (0.1 mol) of 1.5 M solution of BuLi in pentane at −50 °C. After stirring for 1 h, a solution of 20.5 g (0.105 mol) of tosyl chloride in 100 mL of THF was added into the reactor slowly via a dropping funnel while the reaction mixture was still kept at −50 °C with an acetone/dry ice bath. The mixture was then transferred into a separation funnel containing ~400 mL of ice/water. The organic layer was separated, and the aqueous phase was extracted with pentane several times. The combined organic phase was washed with water and dried over anhydrous $MgSO_4$ overnight. After purification by distillation over calcium hydride, the product (1-cholo-1-octyne) was obtained as colorless liquid in 60% yield (8.6 g). IR (KBr), ν (cm^{-1}): 2932 (CH_3), 2860 (CH_2), 2244 ($C{\equiv}C$), 726 ($C{-}Cl$). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 2.2 (t, 2H, $CH_2C{\equiv}$), 1.5 (m, 2H, $CH_2CH_2C{\equiv}$), 1.3 (m, 6H, CH_2), 0.9 (t, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 70.4 ($C{\equiv}$), 57.6 (${\equiv}CCl$).

Instrumentation. The IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker ARX 300 spectrometer. The molecular weights and polydispersity indexes (M_w/M_n) of the polymers were estimated by a Waters Associates gel permeation chromatography (GPC) using degassed THF as eluent (flow rate 1.0 mL/min) and monodisperse polystyrenes (molecular weight range 10^2-10^7) as calibration standards. The UV spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer, and the molar absorptivity (ϵ) of the polymers was calculated on the basis of their repeat units. The specific rotation values of $[\alpha]_D^{25}$ were measured on a Jasco DIP-181 polarimeter. The TGA analysis was performed on a Perkin-Elmer TGA 7 at a heating rate of 20 °C/min in an atmosphere of dry nitrogen.

Polymerization. All the polymerization reactions were carried out in Schlenk tubes with glass stopcocks on sidearms under nitrogen. All the catalysts were handled in open air, except for the $M(CO)_3(NCCH_3)_3$ complexes, which were handled in a dry atmosphere of inert gas. The isolated polymers were carefully purified and characterized, and the analysis data all supported the expected molecular structures of the polymers. Since the characterization data of all the polymers can be found in the literature,[3−5,7,14] we will not repeat reporting the same data in this paper. The synthetic procedure and spectroscopic data of poly(1-cholo-1-octyne) prepared using $Mo(CO)_4(nbd)$ as catalyst in this study is given below as a demonstrative example.

To a Schlenk tube was added 15 mg (0.05 mmol) of $Mo(CO)_4(nbd)$ in air. The catalyst was mixed with 1.0 mL of toluene under nitrogen and aged at 80 °C for 15 min in an oil bath. A solution of 0.2 mL (180 mg, 1.25 mmol) 1-cholo-1-octyne in 1.3 mL of toluene was then added dropwise by a syringe. After stirring the mixture at 80 °C for 1 h, the polymerization reaction was stopped by the addition of a small amount of methanol. The polymer solution was dropped into 200 mL of methanol via a cotton filter under stirring. The precipitated polymer was filtered, washed with methanol for several times, and dried under vacuum at room temperature to a constant weight. The polymeric product was isolated as yellowish fiber in 94% yield (170 mg). $M_w = 248\,500$, $M_w/M_n = 4.1$ (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 2958 (CH_3), 2838 (CH_2), 726 ($C{-}Cl$). UV (dichloromethane), λ_{max}: 244 nm, ϵ_{max}: 4500 mol^{-1} L cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 2.2 (2H, ${=}CCH_2$), 1.3 (8H, CH_2), 0.9 (3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 134.2 (${=}CCl$), 127.5 (${=}C$), 32.4 ($CH_2CH_2CH_3$), 32.3 (${=}CCH_2CH_2CH_2$), 30.4 (${=}CCH_2CH_2$), 23.3 (CH_2CH_3), 14.7 (CH_3).

Results and Discussion

Polymerizations of Nonpolar Acetylenes Catalyzed by Metal Carbonyl Complexes. In our previous reports, we briefly described the catalytic behaviors of the $M(CO)_3(NCCH_3)_3$ complexes in the polymerizations of three acetylene monomers.[7] To check the generality of the catalytic activity, in this work, we further investigated polymerizations of different kinds of acetylene monomers in the presence of the metal carbonyl complexes.

When a CCl_4 solution of a monosubstituted acetylene, *tert*-butylacetylene, was added into a mixture of $Mo(CO)_3(NCCH_3)_3$ in the same solvent, the metal complexes initially suspended in the solvent gradually dissolved in a few minutes, after which the content in the Schlenk tube quickly solidified. The polymer was obtained in quantitative yield (Table 1, no. 1), and the purified product was fibrous in shape and white in color. The dissolution of the polymer took a very long time (>1 week), giving a viscous solution even at a low concentration. The estimation of its molecular weight by GPC, however, failed because the polymer solution could not pass through the guard filter of the GPC

Table 1. Polymerization of Substituted Acetylenes Catalyzed by $M(CO)_3(NCCH_3)_3$ in CCl_4[a]

no.	M	monomer	polymer yield (%)	M_w[b]/10^3	M_w/M_n[b]
1	Mo	$HC\equiv CC(CH_3)_3$	100	*c*	*c*
2	W	$HC\equiv CC(CH_3)_3$	33	134	1.8
3	Mo	$HC\equiv CCH_2Cl$	32	7	1.5
4	Mo	$HC\equiv CCH[Si(CH_3)_3]C_5H_{11}$	88	150	2.1
5	Mo	(−)-$HC\equiv CCH(Si^*R_3)C_5H_{11}$ [d]	64[e]	10	1.9
6	Mo	$HC\equiv CCH[Si(CH_3)_3]C_7H_{15}$	82	117	2.1
7	W	$HC\equiv CCH[Si(CH_3)_3]C_7H_{15}$	12	23	2.3
8	Mo	$HC\equiv CC_6H_4$-*o*-C_6H_{13}	100	145	1.6
9	W	$HC\equiv CC_6H_4$-*o*-C_6H_{13}	89	102	2.3
10	Mo	$HC\equiv CC_6H_4$-*o*-$Si(CH_3)_3$	86	948	2.7
11	W	$HC\equiv CC_6H_4$-*o*-$Si(CH_3)_3$	100	2000	3.8
12	Mo	$HC\equiv CC_6H_4$-*o*-CF_3	85	351	1.7
13	W	$HC\equiv CC_6H_4$-*o*-CF_3	100	179	1.8
14	Mo	$CH_3C\equiv CC_7H_{15}$	24	470	2.2
15	Mo	$CH_3C\equiv CSC_6H_{13}$	75	164	7.5
16	Mo	$CH_3C\equiv CSC_8H_{17}$	76	186	6.4

[a] Carried out under nitrogen at room temperature for 24 h; $[M]_0 = 1.0$ M, [cat.] = 20 mM. [b] Estimated by GPC on the basis of a polystyrene calibration. [c] The polymer solution could not pass through the guard filter of the GPC system, suggesting that the molecular weight of the polymer is extremely high. [d] Si^*R_3 = 1-naphthylphenylmethylsilyl, $[\alpha]_D^{25}$ −9.5° (*c* 11.05, cyclohexane). [e] $[\alpha]_D^{25}$ −98° (*c* 2.33, dioxane).

Table 2. Polymerization of Substituted Acetylenes Catalyzed by $M(CO)_3$(mes) in CCl_4[a]

no.	M	monomer	temp (°C)	polymer yield (%)	M_w[b]/10^3	M_w/M_n[b]
1	Mo	(−)-$HC\equiv CCH(Si^*R_3)$-C_5H_{11}[c]	50	85[d]	17	2.6
2	W	$HC\equiv CC_6H_4$-*o*-$Si(CH_3)_3$	rt	28	17900	8.1
3	Mo	$HC\equiv CC_6H_4$-*o*-$Si(CH_3)_3$	80	40	274	2.3
4	W	$HC\equiv CC_6H_5$	60	100	674	3.1
5	W	$C_2H_5C\equiv CC_6H_5$	80	3	56	2.7

[a] Carried out under nitrogen for 24 h (72 h for no. 1); $[M]_0 = 1.0$ M, [cat.] = 20 mM. [b] Estimated by GPC on the basis of a polystyrene calibration. [c] Si^*R_3 = 1-naphthylphenylmethylsilyl, $[\alpha]_D^{25}$ −9.5° (c 11.05, cyclohexane). [d] $[\alpha]_D^{25}$ −95° (c 1.05, dioxane).

Table 3. Polymerization of Phenylacetylene Catalyzed by $M(CO)_xL_y$ in CCl_4[a]

no.	catalyst[b]	temp (°C)	polymer yield (%)	M_w[c]/10^3	M_w/M_n[c]
1	$W(CO)_4(CH_2PPh_2)_2$	60	0		
2	$[W(CO)_3cp]_2$	60	0		
3	$[Mo(CO)_3cp]_2$	rt	2	41	1.8
4	$[Mo(CO)_3cp]_2$	60	7	9	1.7
5	$Mo(CO)_4$(nbd)	rt	52	36	2.3

[a] Carried out in an atmosphere of dry nitrogen for 24 h; $[M]_0 = 0.5$ M, [cat.] = 20 mM. [b] Abbreviations: Ph = phenyl, cp = cyclopentadiene, nbd = 2,5-norbornadiene, mes = mesitylene. [c] Estimated by GPC on the basis of a polystyrene calibration.

system, although the polymer solution was homogeneous and could be cast into mechanically strong thin films. The W complex was, however, not so effective, producing a poly(*tert*-butylacetylene) in only 33% yield.

Although the Mo complex is an excellent catalyst for the *tert*-butylacetylene polymerization, it failed to convert propargyl chloride into high molecular weight polymer, probably because part of the propargylic structure was isomerized to the corresponding allenic structure,[7,13,15] which served as an inhibiting impurity, hampering the propagation of the acetylene polymerization.

The silicon-containing monosubstituted alkynes were well polymerized by the Mo carbonyl complexes (Table 1, nos. 4−6). A chiral acetylene with a specific rotation of −9.5° was polymerized to an optically active polyacetylene with a much higher $[\alpha]^{25}_D$ value (−98°; Table 1, no. 5), suggesting that the bulky chiral pendants have forced the polyacetylene backbone to take a helical conformation.[2,3,7,12] All the phenylacetylene derivatives underwent efficient polymerizations in the presence of the Mo and W catalysts (Table 1, nos. 8−13). It is noteworthy that the polymerization of the *o*-(trimethylsilyl)phenylacetylene catalyzed by the W complex produces a polymer with an extremely high molecular weight (2.0×10^6) in a quantitative yield.

We also checked whether the $M(CO)_3(NCCH_3)_3$ complexes could initiate polymerizations of disubstituted acetylenes. While the W complexes failed to polymerize 2-decyne, its Mo counterpart effected the acetylene polymerization, giving a high molecular weight poly(2-decyne), albeit in a relatively low yield (Table 1, no. 14). The Mo catalyst was tolerant of the thio group and effectively initiated the polymerizations of 1-alkylthio-1-propynes.

It thus becomes clear that the $M(CO)_3(NCCH_3)_3$ complexes are a group of general catalysts for the polymerizations of different acetylene monomers. The drawback of these complexes is their high sensitivity to air and moisture. We then turn our attention to more stable arene complexes of the metal carbonyls, $M(CO)_3$(mes), which are commercially available and can be handled in open air.

The polymerization of the chiral silicon-containing acetylene monomer catalyzed by the $Mo(CO)_3$(mes) complex again yielded a polymer of high optical activity (Table 2, no. 1). The $W(CO)_3$(mes) complex initiated the polymerization of *o*-(trimethylsilyl)phenylacetylene at room temperature, giving a polymer with an extremely high molecular weight ($\sim 1.8 \times 10^7$), although in only moderate yield. The polymerization of phenylacetylene catalyzed by the W complex at 60 °C produced a high molecular weight polymer in quantitative yield. The result of the polymerization of a disubstituted acetylene, 1-phenyl-1-butyne, in the presence the W complex was, however, disappointing (Table 2, no. 5).

Since $W(CO)_3$(mes) gave excellent result in the polymerization of phenylacetylene, we checked whether other stable W carbonyl complexes could also initiate the phenylacetylene polymerization under similar conditions. Unfortunately, however, none of the W complexes we tested gave any trace amounts of polymeric products (Table 3, nos. 1 and 2). The dimeric $[Mo(CO)_3cp]_2$ complex polymerized phenylacetylene, but the polymer yields were really poor. The result of the polymerization initiated by $Mo(CO)_4$(nbd) complex at room temperature was, however, quite encouraging, giving a poly(phenylacetylene) with a high molecular weight in good yield (Table 3, no. 5).

Polymerizations of Functional Acetylenes Catalyzed by Metal Carbonyl Complexes. Among the metal carbonyl complexes we tested, $W(CO)_3$(mes) and $Mo(CO)_4$(nbd) are the most promising initiators in terms of environmental stability and catalytic activity. All the monomers polymerized by the $W(CO)_3$(mes) and $Mo(CO)_4$(nbd) complexes were nonpolar acetylenes, and it would be nice if these stable complexes can also initiate polymerizations of substituted acetylenes with polar groups, given the importance of functional polyacetylenes in the development of advanced polymeric materials. During our research program on the development of liquid crystalline, light-emitting, and photocon-

Table 4. Polymerization of Functional Acetylenes Catalyzed by $W(CO)_3(mes)$ (W) and $Mo(CO)_4(nbd)$ (M) in CCl_4[a]

no.	cat.	monomer[b]	polymer yield (%)	M_w[c]/10^3	M_w/M_n[c]
1	W	$HC\equiv C(CH_2)_3OCO-Biph-OC_7H_{15}$	36	16	1.6
2	M	$HC\equiv C(CH_2)_3OCO-Biph-OC_7H_{15}$	38	12	1.4
3	W	$HC\equiv C(CH_2)_3CO_2-Biph-OC_7H_{15}$	6	14	1.8
4	M	$HC\equiv C(CH_2)_3CO_2-Biph-OC_7H_{15}$	42	10	1.6
5	W	$HC\equiv C(CH_2)_3O-Biph-OCOC_{11}H_{23}$	64	16	1.7
6	M	$HC\equiv C(CH_2)_3O-Biph-OCOC_{11}H_{23}$	37	13	1.7
7	W	$HC\equiv C(CH_2)_4OCO-Biph-OCOC_{11}H_{23}$	52	17	1.6
8	M	$HC\equiv C(CH_2)_4OCO-Biph-OCOC_{11}H_{23}$	41	13	1.4
9	W	$HC\equiv C(CH_2)_2CO_2(CH_2)_6OCO-Biph-OC_9H_{19}$	56	15	1.5
10	M	$HC\equiv C(CH_2)_2CO_2(CH_2)_6OCO-Biph-OC_9H_{19}$	15	14	1.3
11	W	$HC\equiv C(CH_2)_8CO_2(CH_2)_6OCO-Biph-OC_9H_{19}$	20	23	2.0
12	M	$HC\equiv C(CH_2)_8CO_2(CH_2)_6OCO-Biph-OC_9H_{19}$	14	17	1.5
13	W	$HC\equiv C(CH_2)_3CO_2(CH_2)_6O-Biph-OC_6H_{13}$	31	10	2.5
14	M	$HC\equiv C(CH_2)_3CO_2(CH_2)_6O-Biph-OC_6H_{13}$	31	9	1.9
15	W	$HC\equiv C(CH_2)_8CO_2(CH_2)_6O-Biph-OC_6H_{13}$	78	12	3.0
16	M	$HC\equiv C(CH_2)_8CO_2(CH_2)_6O-Biph-OC_6H_{13}$	54	7	1.9
17	W	$HC\equiv C(CH_2)_8CO_2-Biph-CN$	36	31	1.6
18	M	$HC\equiv C(CH_2)_8CO_2-Biph-CN$	16	11	1.6

[a] Carried out in an atmosphere of dry nitrogen at 60 °C for 24 h; $[M]_0 = 0.2$ M, [cat.] = 10 mM; mes = mesitylene, nbd = 2,5-norbornadiene. [b] Biph = 4,4′-biphenylyl. [c] Estimated by GPC on the basis of a polystyrene calibration.

ductive polyacetylenes, we have synthesized a large variety of functional acetylene monomers.[3,14] Using these acetylenes as model monomers, we checked the functionality tolerance of the $W(CO)_3(mes)$ and $Mo(CO)_4(nbd)$ complexes.

The $W(CO)_3(mes)$ complex polymerized a substituted acetylene with both ester and ether functional groups to a polymer with a narrow molecular weight distribution (as reflected by its low polydispersity index) in a moderate yield (Table 4, no. 1). Similar results were obtained when the $Mo(CO)_4(nbd)$ complex was used as the catalyst. While the monomer with the (oxy)carbonyl (OCO) ester group exhibited the similar polymerizability in the presence of the W and Mo complexes (Table 4, nos. 1 and 2), its cousin with a (carbonyl)oxy (CO_2) ester group polymerized differently, with the Mo complex performing better than its W counterpart (Table 4, nos. 3 and 4).

Changing the position of the ester and ether groups (Table 4, nos. 5 and 6 vs nos. 1 and 2) and increasing the number of the ester groups (Table 4, nos. 7 and 8) in the acetylene monomers did not affect the catalytic activity of the metal complexes to a large extent, although the W complex gave somewhat better results than did its Mo cousin. For the monomers with 2 ester and 1 ether groups (Table 4, nos. 9−12) and those with 1 ester and 2 ether groups (Table 4, nos. 13−16), the $W(CO)_3(mes)$ catalyst generally performed better than did the $Mo(CO)_4(nbd)$ catalyst. A similar trend was observed in the polymerizations of the monomer with ester and cyano groups. The polar cyano group is reactive and often deactivates organometallic catalysts. The fact that the cyano-containing acetylene can be polymerized is thus remarkable, which demonstrates the high tolerance of the metal carbonyl catalysts to polar functional groups.

Most of the polymers obtained from the metal carbonyl-catalyzed polymerizations showed narrow molecular weight distributions. In the best cases, the polydispersity index was as low as 1.3 (Table 4, no. 10), and the polymer yield was as high as 78% (Table 4, no. 15). Optimization of the reaction conditions may lead to the development of living polymerizations of the functional acetylenes, which is currently pursued in our laboratory.

Table 5. Polymerization of Phenylacetylene Catalyzed by $MI_2(CO)_3(NCCH_3)_2$[a]

no.	M	solvent	temp (°C)	time (h)	polymer yield (%)	M_w[b]/ 10^3	M_w/ M_n[b]
1	Mo	CCl_4	50	24	13	3	1.5
2	Mo	toluene	rt	24	15	12	2.7
3	W	CCl_4	50	24	1	7	2.4
4	W	toluene	rt	48	3	22	2.2
5	W	toluene	rt	72	13	19	2.7
6	W	toluene	55	48	9	21	2.8

[a] Carried out under nitrogen; $[M]_0 = 0.5$ M, [cat.] = 20 mM. [b] Estimated by GPC on the basis of a polystyrene calibration.

Polymerizations of Phenylacetylene Catalyzed by Iodine-Containing Metal Carbonyl Complexes. All the polymerizations discussed above gave best results in CCl_4; the reactions carried out in nonhalogenated organic solvents such as toluene and dioxane either completely failed or yielded little amounts of polymeric products. This suggests that the metal carbonyl complexes are activated by the chlorine species provided by the CCl_4 solvent. We thus tried to incorporate halogen atoms into the metal complexes, in the hope that the halogen-containing complexes will initiate the acetylene polymerizations in nonhalogenated solvents.

It is known that the $M(CO)_3(NCCH_3)_3$ complexes can readily react with halogens X_2 (X = Cl, Br, I) to afford seven-coordinated complexes $MX_2(CO)_3(NCCH_3)_2$.[11] The chloro complexes are extremely moisture-sensitive, and the bromo complexes are not stable either. The iodo complexes are, however, quite stable. We thus used the iodine-containing metal carbonyl complexes for acetylene polymerization, with a special attention to their catalytic activity in the polymerizations carried out in nonhalogenated solvents.

The $MoI_2(CO)_3(NCCH_3)_2$ complex polymerized phenylacetylene in CCl_4 to an oligomer with an M_w of 3000 in 13% yield (Table 5, no. 1). In the nonhalogenated solvent of toluene, the complex was also catalytically active and initiated the phenylacetylene polymerization at room temperature. While in CCl_4 the W complex was an extremely poor catalyst for the phenylacetylene polymerization, it gave better results when the polymerizations were carried out in toluene (Table 5, nos. 4−6 vs no. 3).

Thus, the iodine-containing metal carbonyl complexes can initiate phenylacetylene polymerization in a nonhalogenated solvent, although much needs to be done

Table 6. Polymerization of 1-Chloro-2-phenylacetylene Catalyzed by $Mo(CO)_xL_y$[a]

no.	catalyst	solvent	temp (°C)	polymer yield (%)	M_w[b]/10^3	M_w/M_n[b]
1	$Mo(CO)_3(NCCH_3)_3$	CCl_4	rt	28	188	2.1
2	$Mo(CO)_3(NCCH_3)_3$	toluene	rt	29	154	1.9
3	$Mo(CO)_3(NCCH_3)_3$	toluene	60	45	121	2.0
4	$Mo(CO)_3(mes)$[c]	CCl_4	80	91	335	2.2
5	$Mo(CO)_3(mes)$[c]	toluene	80	89	378	1.5

[a] Carried out under nitrogen for 24 h; $[M]_0 = 1.0$ M, [cat.] = 20 mM. [b] Estimated by GPC on the basis of a polystyrene calibration. [c] mes = mesitylene.

to improve the performance of the catalysts. Better design in the ligand structure of the metal carbonyl complexes may lead to the development of catalysts with better environmental stability and catalytic activity.[9]

Polymerizations of Chlorine-Containing Acetylenes Catalyzed by Metal Carbonyl Complexes. What would happen if we incorporate the halogen atoms into the monomer structures? Will the halogenated monomers undergo polymerization in nonhalogenated solvents? To answer these questions, we prepared two chlorine-containing acetylene monomers, 1-chloro-2-phenylacetylene ($ClC{\equiv}CC_6H_5$) and 1-chloro-1-octyne ($ClC{\equiv}CC_6H_{13}$), and investigated their polymerization behaviors in the presence of the nonhalogenated metal carbonyl complexes.

The $Mo(CO)_3(NCCH_3)_3$ complex polymerized 1-chloro-2-phenylacetylene in CCl_4 to give a polymer with a high molecular weight ($\sim 200 \times 10^3$) in a moderate yield (Table 6, no. 1). Comparable results were obtained when the polymerizations were carried out in toluene. When $Mo(CO)_3(mes)$ was used as the catalyst, similar results were again obtained for the polymerizations conducted in CCl_4 and toluene, although in these cases the polymer yields were much higher (~90%; Table 6, nos. 4 and 5). These results suggest that the metal carbonyl complexes can be activated by the chlorine species provided by the monomer, which in turn initiates the acetylene polymerization in the nonhalogenated solvent.

The $Mo(CO)_3(NCCH_3)_3$ complex performed well in the polymerization of 1-chloro-1-octyne in CCl_4, and similar results were obtained in toluene (Table 7, nos. 1 and 2). The polymerization catalyzed by $Mo(CO)_3(mes)$ at 75 °C gave excellent results: it produced a polymer with a very high molecular weight ($\sim 900 \times 10^3$) in almost quantitative yield. The polymerization initiated by $Mo(CO)_3(nbd)$ at room temperature was slow, and the polymer yield was only 28% after 72 h polymerization. At elevated temperature (80 °C), however, the polymerization proceeded faster, and a high molecular weight polymer was obtained in quantitative yield after 24 h polymerization (Table 7, no. 6). Detailed investigation revealed that the polymerization actually finished in ~6 h, at which point the polymer yield reached 100%, and the molecular weight of the polymer approached an almost constant value (Figure 1).

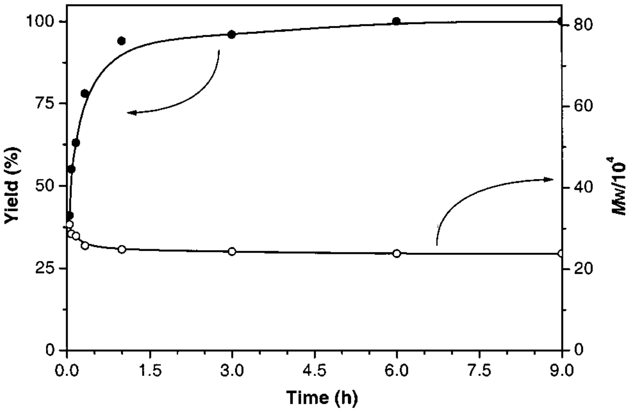

Figure 1. Time course of polymerization of 1-chloro-1-octyne catalyzed by $Mo(CO)_4(nbd)$ in toluene at 80 °C; $[M]_0 = 0.5$ M, [cat.] = 20 mM.

The $Mo(CO)_3(nbd)$ complex also initiated the polymerization of 1-chloro-1-octyne in dioxane, although in a slow rate. Much to our surprise, the monomer underwent polymerization in the presence of $Mo(CO)_6$ in toluene, giving a high molecular weight polymer in a high yield (Table 7, no. 9). The $Mo(CO)_6$ complex is normally activated by UV irradiation in CCl_4;[4d,e] it otherwise hardly acts as a catalyst for acetylene polymerization. What we demonstrated here is that an untreated $Mo(CO)_6$ can be an excellent catalyst in a nonhalogenated solvent, provided it can get the needed chlorine species from other sources (in this case, from the monomer). The polymerization mechanism may possibly consist of the following steps: (i) abstraction of a chlorine from the monomer by the $Mo(CO)_6$ complex, (ii) reaction of the resultant $MO(CO)_5Cl$ complex with the fragment of the monomer to form a carbene species, and (iii) initiation of the metathesis polymerization of the acetylene monomer by the carbene species.[4,5,9,16]

The spectroscopic data of the chlorine-containing polyacetylenes prepared by the metal carbonyl catalysts were identical to those of the polymers prepared by the "classic" metathesis catalysts of metal halides such as $MoCl_5$ (see Experimental Section for the numerical analytic data, the original spectra being given elsewhere[4e]). This suggests that only a tiny fraction of the monomer molecules have participated in the formation of the active catalytic species while the molecules participated in the formation of the polymer chains are the "intact" monomers.

The instability of poly(vinyl chloride)[17] makes people naturally suspect that the chlorine-containing polyacetylenes may not be stable. We thus heated the

Table 7. Polymerization of 1-Chloro-1-octyne Catalyzed by $Mo(CO)_xL_y$[a]

no.	catalyst	solvent	temp (°C)	time (h)	polymer yield (%)	M_w[b]/10^3	M_w/M_nc[b]
1	$Mo(CO)_3(NCCH_3)_3$	CCl_4	rt	24	80	855	1.8
2	$Mo(CO)_3(NCCH_3)_3$	toluene	rt	24	70	400	1.7
3	$Mo(CO)_3(mes)$	toluene	75	24	99	883	2.2
4	$Mo(CO)_4(nbd)$	toluene	rt	24	13	103	2.3
5	$Mo(CO)_4(nbd)$	toluene	rt	72	28	97	2.3
6	$Mo(CO)_4(nbd)$	toluene	80	24	100	238	4.9
7	$Mo(CO)_4(nbd)$	dioxane	80	72	25	54	4.4
8	$Mo(CO)_5(PPh_3)$	CCl_4	80	24	11	302	1.9
9	$Mo(CO)_6$	toluene	80	72	91	317	2.6

[a] Carried out in an atmosphere of dry nitrogen; $[M]_0 = 0.5$ M, [cat.] = 20 mM; mes = mesitylene, nbd = 2,5-norbornadiene. [b] Estimated by GPC on the basis of a polystyrene calibration.

Table 8. Thermal Stability of Substituted Polyacetylenes[a]

	$-(RC{=}CR')_n-$					
no.	R	R′	temp (°C)	time (h)	$\alpha \times 10^3$	ref
1	Cl	C_6H_{13}	130	24	0.01	this work
2	CH_3	C_5H_{11}	120	20	51	18
3	Cl	Ph	120	20	~0	this work, 18
4	CH_3	Ph	120	20	0.23	18

[a] The polymer samples were heated in the air at the given temperatures for the given periods of time.

polymers at elevated temperatures (>100 °C) but found little change in their molecular weights. For example, after heating at 130 °C for 24 h, the M_n of a poly(1-chloro-1-octyne) changed from 49 560 to 49 340. TGA analysis revealed that a 5% weight loss of the polymer occurred at a temperature as high as ~330 °C.

We used a chain scission probability parameter α^{18} to compare the thermal stability of the chlorine-containing polyacetylenes with that of other polyacetylene cousins. The α value of poly(1-chloro-1-octyne) was as low as 1×10^{-5} (Table 8, no. 1); this is, after 24 h treatment at 130 °C, there was on the average only 1 bond scission in every 10^5 bonds in the polymer chain. A polyacetylene of similar structure, i.e., poly(2-octyne), had an α value as high as 5100×10^{-5}. Thus, the incorporation of the chlorine pendants into the polyacetylene backbone actually increased, instead of decreasing, the thermal stability of the polymer. Similarly, poly(1-chloro-2-phenylacetylene) exhibited a lower α value or higher thermal stability than its nonhalogenated cousin, poly(1-phenyl-1-propyne) (Table 8, nos. 3 and 4).

Conclusion

In this work, we have explored new catalysts for acetylene polymerization from transition metal carbonyl complexes. We have found that (1) the $M(CO)_3(NCCH_3)_3$ complexes are a group of general catalysts for acetylene polymerization under mild conditions without pre-UV irradiation, (2) the $M(CO)_3$(mes) and $Mo(CO)_3$(nbd) complexes can effect polymerizations of acetylenes with both nonpolar and polar functional groups, (3) the performance of the $MI_2(CO)_3(NCCH_3)_2$ catalysts in the nonhalogenated solvent (toluene) is better than in the halogenated solvent (CCl_4), and (4) the Mo carbonyl complexes can initiate polymerizations of the chlorine-containing acetylene monomers in nonhalogenated solvents.

Except for the $M(CO)_3(NCCH_3)_3$ complexes, all the other metal carbonyl complexes developed in this study are environmentally stable and can be handled with ease in open air. All the catalysts are single-component systems without any additives, obviating the trouble of preparing binary and ternary mixtures of catalyst solutions. Such stable and simple catalysts are of practical value and may find industrial applications.

Acknowledgment. The work described in this paper was partially supported by the grants of the Research Grants Council of the Hong Kong Special Administrative Region, China (Project Nos. HKUST6187/99P, 6062/98P, 6149/97P, and 597/95P). This project has also benefited from the support of Technology Resources International (TRI) Corporation, Georgia. We thank the Central Research Laboratory of the NEOS Co., Ltd. (Japan), and the Shanghai Institute of Organic Chemistry (China) for their advice and assistance in fluorine chemistry. We also thank Dr. K. C. Su of TRI, Drs. T. Monde and F. Nemoto of NEOS, Mr. N. Kotera of Sumitomo Chemical Co., Ltd., and Dr. H. Xue of the Biochemistry Department of our university for their helpful discussions.

References and Notes

(1) For reviews and monographs, see: (a) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998. (b) *Conjugated Conducting Polymers*; Kiess, H. G., Ed.; Springer-Verlag: Berlin, 1992. (c) Gorman, C. B.; Grubbs, R. H. In *Conjugated Polymers*; Bredas, J. L., Silbey, R., Eds.; Kluwer Academic: Dordrecht, 1991; p 1.

(2) E.g.: (a) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449. (b) Vohlidal, J.; Sedlacek, J.; Patev, N.; Lavastre, O.; Dixneuf, P. H.; Cabioch, S.; Balcar, H.; Pfleger, J.; Blechta, V. *Macromolecules* **1999**, *32*, 6439. (c) Nakako, H.; Nomura, R.; Tabata, M.; Masuda, T. *Macromolecules* **1999**, *32*, 2861. (d) Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. *Science* **1998**, *282*, 1683. (e) Choi, S. K.; Lee, J. H.; Kang, S. J.; Jin, S. H. *Prog. Polym. Sci.* **1997**, *22*, 693. (f) Tada, K.; Hidayat, R.; Teraguchi, M.; Masuda, T.; Yoshino, K. *Jpn. J. Appl. Phys.* **1996**, *35*, L1138. (g) Aoki, T.; Shinohara, K.; Kaneko, T.; Oikawa, E. *Macromolecules* **1996**, *29*, 4192. (h) Nishide, H.; Keneko, T.; Igarashi, M.; Tsuchida, E.; Yoshioka, N.; Lahti, P. M. *Macromolecules* **1994**, *27*, 3082. (i) Le Moigne, J.; Hilberer, A.; Strazielle, C. *Macromolecules* **1992**, *25*, 6705. (j) Moore, J. S.; Gorman, C. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 1704. (k) Kang, E. T.; Ehrlich, P.; Bhatt, A. P.; Anderson, W. A. *Macromolecules* **1984**, *17*, 1020. (l) Ciardelli, F.; Lanzillo, S.; Pieroui, O. *Macromolecules* **1974**, *7*, 174.

(3) (a) Tang, B. Z.; Chen, H. Z.; Xu, R. S.; Lam, J. W. Y.; Cheuk, K. K. L.; Wong, H. N. C.; Wang, M. *Chem. Mater.* **2000**, *12*, 213. (b) Kong, X.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* **1999**, *32*, 1722. (c) Huang, Y. M.; Lam, J. W. Y.; Cheuk, K. K. L.; Ge, W.; Tang, B. Z. *Appl. Phys. Lett.* **1999**, *75*, 4094. (d) Lee, C. W.; Wong, K. S.; Lam, W. Y.; Tang, B. Z. *Chem. Phys. Lett.* **1999**, *307*, 67. (e) Tang, B. Z.; Poon, W. H.; Peng, H.; Wong, H. N. C.; Ye, X.; Monde, T. *Chin. J. Polym. Sci.* **1999**, *17*, 81. (f) Kong, X.; Tang, B. Z. *Chem. Mater.* **1998**, *10*, 3352. (g) Tang, B. Z.; Kong, X.; Wan, X.; Peng, H.; Lam, W. Y.; Feng, X.; Kwok, H. S. *Macromolecules* **1998**, *31*, 2419. (h) Lam, J. W. Y.; Cheuk, K. K. L.; Tang, B. Z. *Polym. Prepr.* **2000**, *41* (1), 912. (i) Cheuk, K. K. L.; Lam, J. W. Y.; Tang, B. Z. *Polym. Mater. Sci. Eng.* **2000**, *82*, 56.

(4) For reviews and monographs, see: (a) *Metathesis Polymerization of Olefins and Polymerizations of Alkynes*; Imamoglu, Y., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1998. (b) Ginsburg, E. J.; Gorman, C. B.; Grubbs, R. H. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: New York, 1995; p 353. (c) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (d) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1987**, *81*, 121. (e) Tang, B. Z.; Xu, K.; Sun, Q.; Lee, P. P. S.; Peng, H.; Salhi, F.; Dong, Y. In *Transition Metal Catalysis in Macromolecular Design*; Bofa, L. S., Novak, B. M., Eds.; American Chemical Society: Washington, DC, 2000; Chapter 9, pp 146−164.

(5) (a) Masuda, T.; Kuwane, Y.; Yamamoto, K.; Higashimura, T. *Polym. Bull.* **1980**, *2*, 823. (b) Landon, S. J.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 6739.

(6) (a) Calderazzo, F.; Ercoli, R.; Natta, G. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Piero, P., Eds.; Wiley: New York, 1968; Vol. 1, Chapter 1. (b) Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297.

(7) (a) Tang, B. Z.; Kotera, N. *Macromolecules* **1989**, *22*, 4388. (b) Tang, B. Z.; Kotera, N. Jpn Patent H2-258807, 1990. (c) *Adv. Mater.* **1990**, *2*, 107.

(8) (a) Shivasubramanian, V.; Sundarajan, G. *J. Mol. Catal.* **1991**, *65*, 205. (b) Ganasamoorthy, S.; Sundarajan, G. *Macromolecules* **1992**, *25*, 2060. (c) Anatharaj, T. A.; Sundarajan, G. *Organometallics* **1997**, *16*, 4940.

(9) (a) Tamura, K.; Masuda, T.; Higashimura, T. *Polym. Bull.* **1993**, *30*, 537. (b) Tamura, K.; Masuda, T.; Higashimura, T. *Polym. Bull.* **1994**, *32*, 289. (c) Tamura, K.; Misumi, Y.; Masuda, T. *Chem. Commun.* **1996**, 373. (d) Masuda, T.; Kaneshiro, H.; Hayano, S.; Misumi, Y.; Bencze, L. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1977.

(10) (a) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem*. **1962**, *1*, 433. (b) Dobson, G. R.; Elsayed, M. F. A.; Stolz, I. W.; Shiline, R. K. *Inorg. Chem*. **1962**, *1*, 526.

(11) Baker, P. K.; Frasher, S. G.; Keys, E. M. *J. Organomet. Chem*. **1986**, *309*, 319.

(12) (a) Lam, J. W. Y.; Cheuk, K. K. L.; Tang, B. Z. *Polym. Prepr*. **2000**, *41* (1), 969. (b) Cheuk, K. K. L.; Lam, J. W. Y.; Sun, Q.; Cha, J. A. K.; Tang, B. Z. *Polym. Prepr*. **1999**, *40* (2), 655. (c) Cheuk, K. K. L.; Lam, J. W. Y.; Sun, Q.; Cha, J. A. K.; Tang, B. Z. *Polym. Prepr*. **1999**, *40* (2), 653. (d) Sun, Q.; Tang, B. Z. *Polym. Prepr*. **1999**, *40* (1), 560. (e) Sun, Q.; Tang, B. Z. *Polym. Prepr*. **1999**, *40* (1), 558.

(13) (a) *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: New York, 1995. (b) Bransma, L.; Verkruijsse, D. H. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elservier: Amsterdam, 1981.

(14) (a) Lam, J. W. Y.; Kong, X.; Dong, Y. P.; Cheuk, K. K. L.; Xu, K.; Tang, B. Z. *Macromolecules* **2000**, *33*, 5027. (b) Lee, P. P. S.; Geng, Y. H.; Kwok, H. S.; Tang, B. Z. *Thin Solid Films* **2000**, *363*, 149. (c) Huang, Y. M.; Lam, J. W. Y.; Cheuk, K. K. L.; Ge, W.; Tang, B. Z. *Macromolecules* **1999**, *32*, 5976. (d) Tang, B. Z.; Xu, H. *Macromolecules* **1999**, *32*, 2569. (e) Tang, B. Z.; Lam, J. W. Y.; Kong, X.; Lee, P. P. S.; Wan, X.; Kwok, H. S.; Huang, Y. M.; Ge, W.; Chen, H.; Xu, R.; Wang, M. In *Liquid Crystals III*; Khoo, I., Ed.; SPIE-The International Society for Optical Engineering: Bellingham, WA, 1999; pp 62−71.

(15) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.

(16) (a) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997. (b) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Boston, 1989.

(17) (a) *Chemistry of Chlorine-Containing Polymers: Syntheses, Degradation, Stabilization*; Zaikov, G. E., Ed.; Nova Science: New York, 2000. (b) *Handbook of Polymer Degradation*; Hamid, S. H., Amin, M. B., Maadhah, A. G., Eds.; Marcel Dekker: New York, 1992.

(18) Masuda, T.; Tang, B. Z.; Higashimura, T.; Yamaoka, H. *Macromolecules* **1985**, *18*, 2369.

MA000843A