blends by adjusting parameters such as the difference between the temperature of polymerization and the T_g of the matrix. At present we have demonstrated that this technique can be used to produce blends of immiscible polymers, in which the domain sizes are limited by the slow kinetics of aggregation within a solid.

Registry No. PS, 9003-53-6; PB, 9003-17-2; V^{III}(acac), 13476-99-8; $Ti(OBu)_4$, 5593-70-4; Et_3Al, 97-93-8.

References and Notes

(1) *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic: New York, 1978; Vol. 1, 2.
(2) *Polymer–Polymer Miscibility*; Oblasi, O., Robeson, L., Eds.; Academic: New York, 1979.
(3) Walsh, D. J.; Higgins, J. S.; Maconnachie, A. *Polymer Blends and Mixtures*; Martinus Nijohoff: Boston, 1985.
(4) Paul, D. R.; Barlow, L. M. *J. Macromol. Sci—Rev. Macromol. Chem.* **1980**, *C18*, 109.
(5) Koningsveld, R.; Kleintjens, L. A.; Schoffeleers, H. M. *Pure Appl. Chem.* **1974**, *39*, 1.
(6) Galvin, M. E.; Wnek, G. E. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2727.
(7) Doube, C. P.; Walsh, D. J. *Polymer* **1979**, *20*, 1115.
(8) Walsh, D. J.; Cheng, C. L. *Polymer* **1984**, *25*, 1023.
(9) Walsh, D. J.; Shan, C. K. *Polymer* **1984**, *23*, 1966.
(10) Yau, H.; Stupp, S. I. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 813.
(11) Buter, R.; Tan, Y. Y.; Challa, G. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 989.
(12) Buter, R.; Tan, Y. Y.; Challa, G. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1003.
(13) Buter, R.; Tan, Y. Y.; Challa, G. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1013.
(14) Buter, R.; Tan, Y. Y.; Challa, G. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 2975.
(15) Galvin, M. E.; Heffner, S. A. *Macromolecules* **1986**, *19*, 2461.
(16) Hirai, H.; Hiraki, K.; Noguchi, I.; Inoue, T.; Makishima, S. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 2393.
(17) *Polymer Handbook*; Brandup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; Vol. 4.
(18) Natta, G.; Porri, L.; Carbonaro, A. *Makromol. Chem.* **1964**, *77*, 126.
(19) Krause, S. *J. Macromol. Sci.—Rev. Macromol. Chem.* **1972**, *7;21*, 251.
(20) Bates, F. S.; Bair, H. E.; Hartney, M. A. *Macromolecules* **1984**, *17*, 1987.
(21) Bucknall, C. B. In *Polymer Blends and Mixtures*; Walsh, D. J., Higgins, J. S., Maconnachie, A., Eds.; Martinus Nijhoff: Boston, 1985; p 349.
(22) Sperling, L. H. In *Polymer Blends and Mixtures*; Walsh, D. J., Higgins, J. S., Maconnachie, A., Eds.; Martinus Nijhoff: Boston, 1985; p 267.

Living Polymerization of 1-Chloro-1-alkynes Catalyzed by $MoCl_5$–n-Bu_4Sn–EtOH

Toshio Yoshimura, Toshio Masuda,* and Toshinobu Higashimura*

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

Received September 28, 1987

ABSTRACT: Polymerization of 1-chloro-1-octyne ($ClC{\equiv}C$-n-C_6H_{13}) catalyzed by a mixture of $MoCl_5$, n-Bu_4Sn, and EtOH (molar ratio 1:1:0.5) produced a polymer with a narrow molecular weight distribution (MWD; $\bar{M}_w/\bar{M}_n$ = 1.1–1.3). The number-average molecular weight ($\bar{M}_n$) of the polymer increased in direct proportion to conversion and further increased on addition of a new monomer feed to the polymerization system. The ratio of the propagating species to the Mo catalyst was rather small (0.017). Other 1-chloro-1-alkynes ($ClC{\equiv}CR$; R = n-C_4H_9, n-C_8H_{17}, and n-$C_{14}H_{29}$) formed polymers with similarly narrow MWDs. Thus, the present polymerization indicates the presence of a long-lived propagating species and, though yet imperfect, is the first clear example of living polymerization of acetylenic monomers.

Introduction

Living polymerization is the polymerization in which termination and chain transfer are absent and is a useful technique for the synthesis of tailor-made polymers such as monodisperse polymers and block copolymers. Whereas the living anionic polymerization has been extensively investigated by Szwarc and other researchers,[1] only a few studies have so far appeared on the living polymerization initiated by transition-metal catalysts, i.e., polymerization of norbornene by Ti, Ta, and W catalysts,[2] polymerization of propene by V catalysts,[3] and polymerization of 1,3-butadiene by Ni catalysts.[4] Though the ring-opening polymerization of cyclooctyne was suggested to be a living system, the polymer did not show a narrow molecular weight distribution.[5] Thus there has been no evident report on the living polymerization of acetylenic monomers to date.

Groups 5 and 6 transition-metal (Nb, Ta, Mo, and W) chlorides work as effective catalysts in the polymerization of various substituted acetylenes.[6] Recently, we reported that 1-chloro-1-alkynes ($ClC{\equiv}CR$; R = n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, and n-$C_{14}H_{29}$), a series of chlorine-containing aliphatic acetylenes, polymerize with Mo catalysts (e.g., $MoCl_5$–n-Bu_4Sn) to give new high-molecular-weight polymers (weight-average molecular weight, $\bar{M}_w$, ca. 2×10^5–2×10^6) in high yields.[7] The molecular weight distributions (MWDs) of the product polymers are, however, rather broad [polydispersity ratio ($\bar{M}_w/\bar{M}_n$) 1.7–2.5].

Mo- and W-catalyzed polymerization of substituted acetylenes and olefin metathesis have many common features (e.g., identical catalysts and cocatalysts effect both reactions). Thus far, a wide variety of catalysts based on W and Mo have been exploited for olefin metathesis.[8-10] Among them, effective catalysts are often composed of three components, that is, WCl_6, an organometallic cocatalyst, and a modifier. A number of oxygen-containing compounds can be the modifier. For instance, Calderon et al. have found that a mixture of WCl_6, $EtAlCl_2$, and ethanol (EtOH) shows high activity for olefin metathesis, whereas this catalyst is less active if it lacks EtOH.[11]

While we were studying how oxygen-containing compounds would affect the polymerization of 1-chloro-1-octyne by the $MoCl_5$-organometallic cocatalyst system, we found that a three-component catalyst composed of $MoCl_5$, n-Bu_4Sn, and EtOH produces a long-lived propagating species.[12] The present paper describes a detailed study on the polymerization of 1-chloro-1-octyne and its homologues by $MoCl_5$–n-Bu_4Sn–EtOH.

Experimental Section

Materials. 1-Chloro-1-alkynes were prepared by lithiation of 1-alkynes, followed by chlorination with tosyl chloride, as described

0024-9297/88/2221-1899$01.50/0

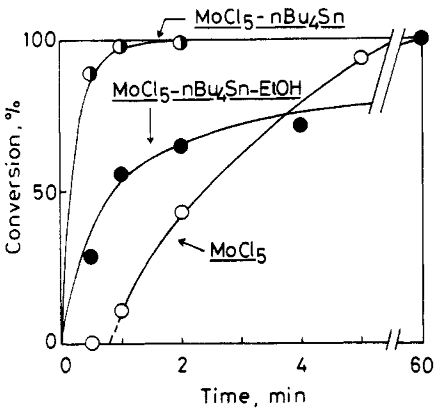

Figure 1. Time–conversion curves for the polymerization of 1-chloro-1-octyne by $MoCl_5$-based catalysts (in toluene, 30 °C, $[M]_0 = 0.50$ M, $[MoCl_5] = [n\text{-}Bu_4Sn] = 20$ mM, $[EtOH] = 10$ mM).

before.[7a] The monomers prepared were distilled twice from calcium hydride before use. Other monomers were prepared or commercially obtained.[6] Their purities were over 99% according to gas chromatography (GC). $MoCl_5$ (Strem Chemicals, purity >99%) and organometallic cocatalysts were commercially obtained and used without further purification. Oxygen-containing compounds such as EtOH were distilled before use. Toluene as polymerization solvent was purified by a standard method.

Procedures. Polymerizations were carried out under dry nitrogen in a baked flask equipped with a three-way stopcock. A typical procedure for the polymerization of 1-chloro-1-octyne is as follows (see Table I, row 4 for results): A monomer solution was prepared by mixing 1-chloro-1-octyne (6.0 mmol, 0.87 g, 0.96 mL), dodecane (0.24 mL, as internal standard for GC), and toluene (4.8 mL) and kept at 30 °C. In a separate flask, $MoCl_5$ (0.20 mmol, 54.6 mg) and n-Bu_4Sn (0.20 mmol, 69.4 mg) were dissolved in toluene (5.0 mL), followed by allowing to stand (aging) at 30 °C for 10 min. To this solution was added EtOH (4.6 mg, 0.10 mmol), and then this catalyst solution was aged at 30 °C for another 10 min. Polymerization was initiated by adding 5 mL of the above monomer solution to the catalyst solution at 30 °C. After 1 h, the polymerization was terminated by adding a mixture (3 mL) of methanol and toluene (1:4 volume ratio). Monomer conversion was determined by measuring the initial and final monomer concentrations by GC (silicone DC 3 m, 150 °C). The polymerization solution was diluted with toluene (20 mL) and poured into methanol (1 L) under stirring. The precipitated polymer was filtered off, washed with methanol, and dried to a constant weight under vacuum. Polymer yield was determined by gravimetry, which agreed with the monomer conversion within an error of 5%.

The MWD curves of polymers were observed by gel permeation chromatography (GPC) using a Jasco Trirotar liquid chromatograph (Shodex A804, A806, and A807 polystyrene gel columns, eluent $CHCl_3$), and the number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$, respectively) of polymers were calculated on the basis of a polystyrene calibration.

Results and Discussion

Polymerization of 1-Chloro-1-octyne by $MoCl_5$-Based Catalysts. 1-Chloro-1-octyne was polymerized in the presence of three kinds of $MoCl_5$-based catalysts, that is, $MoCl_5$ alone, $MoCl_5$–n-Bu_4Sn (1:1), and $MoCl_5$–n-Bu_4Sn–EtOH (1:1:0.5). The polymerizations were carried out in toluene at 30 °C.

Figure 1 illustrates time–conversion curves for the polymerization with the three $MoCl_5$-based catalysts. With all these catalysts, the monomer was completely consumed after 1 h. The polymerization with $MoCl_5$ alone proceeded after a short induction period, and almost all of the monomer was consumed after 5 min. Use of n-Bu_4Sn as cocatalyst eliminated the induction period and accelerated the reaction, so that monomer conversion became virtually quantitative in 1 min. This should be because the cocatalyst helps form a metal carbene (propagating species) readily (see ref 13 in this regard). Further, the polymerization by $MoCl_5$–n-Bu_4Sn–EtOH proceeded smoothly without any induction period, though it was slower than the one by $MoCl_5$–n-Bu_4Sn. This suggests that the addition of EtOH makes the propagating species less active.

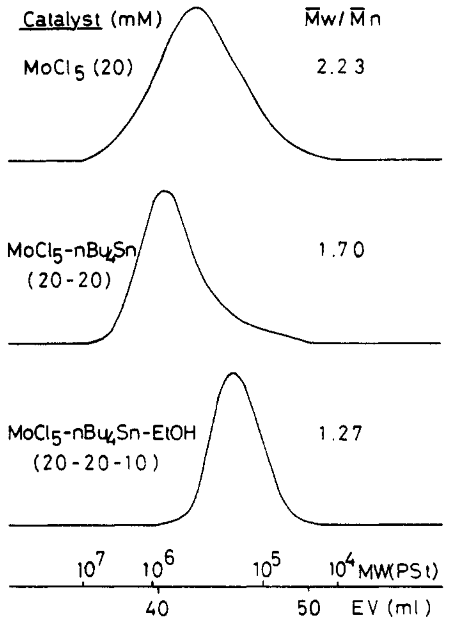

Figure 2. MWD of poly(1-chloro-1-octyne) obtained with $MoCl_5$-based catalysts (polymerized for 1 h under the same conditions as in Figure 1; the monomer conversions are all 100%).

Table I
Polymerization of 1-Chloro-1-octyne by $MoCl_5$-Based Catalysts[a]

catalyst	monomer convn, %	polymer $\bar{M}_n/10^4$	polymer $\bar{M}_w/\bar{M}_n$
$MoCl_5$	100	23	2.23
$MoCl_5$–n-Bu_4Sn	100	46	1.70
$MoCl_5$–EtOH	100	20	2.23
$MoCl_5$–n-Bu_4Sn–EtOH	100	16	1.27
$MoCl_5$–n-Bu_4Sn–EtOH[b]	89	10	1.34
$MoCl_5$–n-Bu_4Sn–EtOH[c]	38	5.3	1.34

[a] Polymerized in toluene at 30 °C for 1 h; $[M]_0 = 0.50$ M, $[MoCl_5] = [n\text{-}Bu_4Sn] = 20$ mM, $[EtOH] = 10$ mM. [b] $[EtOH] = 20$ mM. [c] $[EtOH] = 40$ mM.

The MWD curves of the polymers obtained with the three $MoCl_5$-based catalysts are depicted in Figure 2. $MoCl_5$ alone gave a high-molecular-weight polymer with a broad MWD ($\bar{M}_w/\bar{M}_n \sim 2.2$). The MWD of the polymer obtained with $MoCl_5$–n-Bu_4Sn was narrower ($\bar{M}_w/\bar{M}_n = 1.7$), but it showed a tailing at the lower molecular weight side. The $MoCl_5$–n-Bu_4Sn–EtOH catalyst, in contrast, gave a very narrow MWD ($\bar{M}_w/\bar{M}_n \leq 1.3$), in which no tailing was observed.

Table I lists data for the polymerization of 1-chloro-1-octyne by $MoCl_5$-based catalysts. $MoCl_5$ alone, $MoCl_5$–n-Bu_4Sn (1:1), and $MoCl_5$-EtOH (1:1) as catalysts produced polymers with broad MWDs ($\bar{M}_w/\bar{M}_n = 1.7$–$2.2$). In contrast, when $MoCl_5$–n-Bu_4Sn–EtOH (1:1:0.5) was employed as catalyst, the MWD was much narrower ($\bar{M}_w/\bar{M}_n \leq 1.3$). As the amount of EtOH was increased, the monomer conversion and the $\bar{M}_n$ of polymer decreased, while the MWD hardly changed. Thus, half as much EtOH as $MoCl_5$ and n-Bu_4Sn is adequate to obtain the polymer with a narrow MWD in high yield. A change of the order of addition of the reagents in the catalyst preparation, that is, addition of n-Bu_4Sn to a mixture of $MoCl_5$ and EtOH,

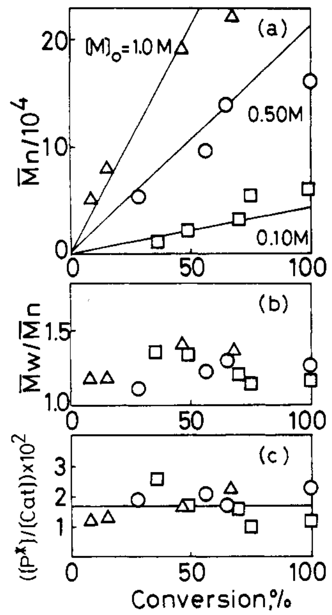

Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and [P*]/[Cat] as functions of conversion in the polymerization of 1-chloro-1-octyne by $MoCl_5$–n-Bu_4Sn–EtOH (1:1:0.5; in toluene, 30 °C, $[MoCl_5]$ = 20 mM, $[M]_0$ as indicated).

caused virtually no difference in catalyst activity and MWD.

Formation of Long-Lived Propagating Species in the Polymerization of 1-Chloro-1-octyne by $MoCl_5$–n-Bu_4Sn–EtOH. Figure 3 shows $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and [P*]/[Cat] as functions of conversion in the polymerization of 1-chloro-1-octyne by $MoCl_5$–n-Bu_4Sn–EtOH (1:1:0.5). Here [P*]/[Cat] is the ratio of the propagating species to the Mo catalyst and calculated from the following equation:

$$[P^*]/[Cat] = [M]_{consumed}/(DP_n[Cat])$$

where DP_n means the number-average degree of polymerization. Three different initital monomer concentrations were employed, and the DP_n determined by GPC was tentatively used for the calculation of [P*]/[Cat]. The $\bar{M}_n$ of polymer increased in direct proportion to conversion at all the monomer concentrations. The MWD remained narrow ($\bar{M}_w/\bar{M}_n$ = 1.1–1.4) irrespective of the conversion and concentration of monomer. The [P*]/[Cat] ratio, however, was no more than ca. 0.02 (the overall average of the values were 0.017). This means that only a few percent of the Mo catalyst is converted into the propagating species. In this connection, it has recently been reported that the amount of the W carbene formed from a mixture of WCl_6 and Me_4Sn is no more than 0.7%.[13] It is noted that the [P*]/[Cat] ratio remains virtually constant throughout the polymerization irrespective of monomer concentration. The lines in Figure 3a stand for the theoretical changes to $\bar{M}_n$ with conversion in the case where [P*]/[Cat] is 0.017.

Control of $\bar{M}_n$ of poly(1-chloro-1-octyne) was tried by changing the monomer-to-catalyst ratio in the feed (Figure 4). The range of monomer concentration is 0.10–1.0 M, and that of catalyst concentration is 5–20 mM in these polymerizations. The $\bar{M}_n$ of produced polymers was virtually proportional to the ratio of $[M]_0/[Cat]$. The $\bar{M}_w/\bar{M}_n$ was close to unity at $[M]_0/[Cat] < 50$, though it gradually increased with increasing $[M]_0/[Cat]$ ratio. Thus it is possible to prepare poly(1-chloro-1-octyne) that has a narrow MWD and a $\bar{M}_n$ in the range of ca. 5×10^4–40×10^4.

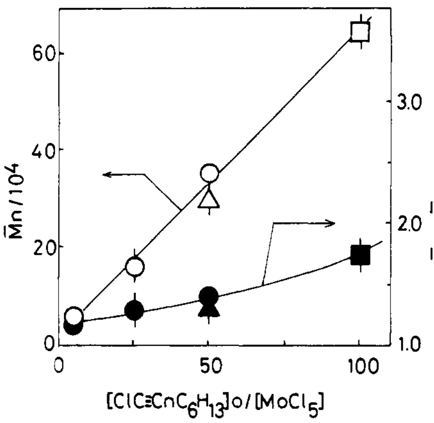

Figure 4. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ as functions of monomer-to-catalyst ratio ($[M]_0/[Cat]$) in the polymerization of 1-chloro-1-octyne by $MoCl_5$–n-Bu_4Sn–EtOH (1:1:0.5) (in toluene, 30 °C, 1 h, $[MoCl_5]$ = 20 mM (○, ●), 10 mM (△, ▲), 5 mM (□, ■); marks with a bar, $[M]_0$ = 0.50 M).

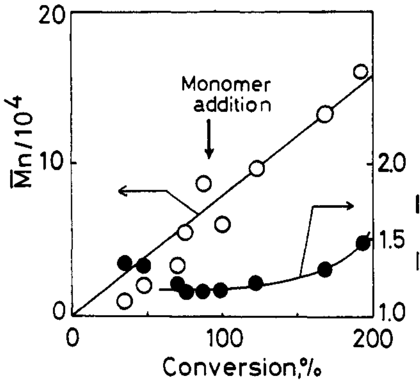

Figure 5. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ as functions of conversion before and after the second monomer addition in the polymerization of 1-chloro-1-octyne by $MoCl_5$–n-Bu_4Sn–EtOH (1:1:0.5; in toluene, 30 °C, $[M]_0 = [M]_{added}$ = 0.10 M, $[MoCl_5]$ = 20 mM).

A proof of living polymerization is that the molecular weight of the formed polymer increases further when additional monomer is supplied to a polymerization system in which all the monomer has been consumed. The "monomer-addition" experiment was carried out to examine whether such a behavior is observed or not, i.e., a new monomer feed in toluene solution was added to the polymerizing mixture when the initial monomer feed had virtually been consumed. The second-stage polymerization also proceeded almost quantitatively after an adequate period of time. The $\bar{M}_n$ of polymer increased proportionally to conversion also in the second stage (Figure 5). The $\bar{M}_w/\bar{M}_n$ ratio of polymer, however, tended to increase at the latter stage. This stems from the appearance of a small shoulder in the MWD curve (Figure 6). Since this shoulder does not shift with conversion, partial deactivation of the propagating species seems responsible. The deactivation might be either spontaneous or due to any impurities contained in the additional monomer feed. Anyhow, the smooth linear increase of $\bar{M}_n$ seen in Figure 5 indicates that almost all the polymer chains formed in the first-stage polymerization resume propagation when an additional monomer feed is supplied.

All of the above-stated results clearly demonstrate the formation of a long-lived propagating species by use of $MoCl_5$–n-Bu_4Sn–EtOH as catalyst.

Effect of Catalyst Components. The catalyst system effective for living polymerization of 1-chloro-1-octyne proved to consist of three components, that is, a transition-metal catalyst ($MoCl_5$), an organometallic cocatalyst

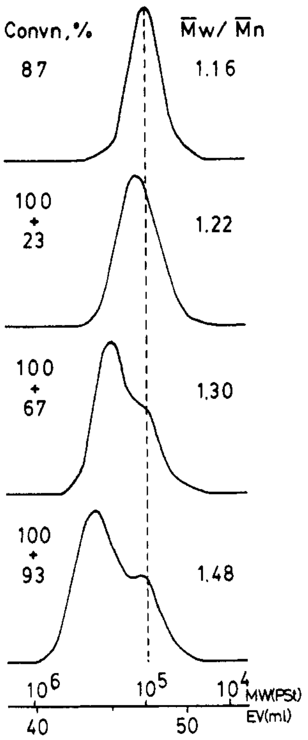

Figure 6. MWD of poly(1-chloro-1-octyne) obtained with $MoCl_5$–n-Bu_4Sn–EtOH (1:1:0.5) before and after the second monomer addition (polymerized under the same conditions as in Figure 5).

Table II
Polymerization of 1-Chloro-1-octyne by $MoCl_5$-Cocatalyst-EtOH (1:1:0.5)[a]

cocatalyst	monomer convn, %	polymer	
		$\bar{M}_n/10^4$	$\bar{M}_w/\bar{M}_n$
none	100	20	2.23
Me_4Sn	100	24	1.89
n-Bu_4Sn	100	16	1.27
Ph_4Sn	0		
Et_3SiH	54	41	1.68
Ph_3SiH	74	15	2.00
Ph_3Bi	0		
Ph_3Sb	17	16	2.36

[a] Polymerized in toluene at 30 °C for 1 h; $[M]_0$ = 0.50 M, $[MoCl_5]$ = 20 mM.

(n-Bu_4Sn), and an oxygen-containing compound (EtOH). Effects of various organometallic cocatalysts and oxygen-containing compounds were examined to elucidate what catalyst systems lead to the living polymerization.

Table II shows the effect of kind of groups 4 and 5 organometallic cocatalysts on the polymerization of 1-chloro-1-octyne by $MoCl_5$–cocatalyst–EtOH (1:1:0.5). As is obvious from Table II, the MWD of the polymer was quite narrow only with n-Bu_4Sn as cocatalyst; none of the other cocatalysts achieved so narrow a MWD. It is thought that the organometallics in Table II work as mild reducing and/or alkylating agents. The observed strong dependence of the MWD of polymer on the kind of cocatalyst implies that a moiety of the cocatalyst remains in the propagating species, which exert a complicated steric effect for the present polymerization. It is, however, not clear at present why n-Bu_4Sn solely satisfies the steric and/or other requirements for the living polymerization.

Table III
Effect of Oxygen-Containing Compounds on the Polymerization of 1-Chloro-1-octyne by $MoCl_5$–n-Bu_4Sn (1:1)[a]

O compd	monomer convn, %	polymer	
		$\bar{M}_n/10^4$	$\bar{M}_w/\bar{M}_n$
none	100	46	1.70
EtOH	100	16	1.27
CH_3COOH	100	12	1.26
CH_3COO-n-Bu	100	15	1.37
acetone	100	14	1.31
H_2O	100	27	1.69

[a] Polymerized in toluene at 30 °C for 1 h; $[M]_0$ = 0.50 M, $[MoCl_5]$ = 20 mM, [O compound] = 10 mM.

Table IV
Polymerization of Various Acetylenes by $MoCl_5$–n-Bu_4Sn–EtOH (1:1:0.5)[a]

monomer	monomer convn, %	polymer	
		$\bar{M}_n/10^4$	$\bar{M}_w/\bar{M}_n$
$ClC{\equiv}C$-n-C_4H_9	100	37	1.34
$ClC{\equiv}C$-n-C_6H_{13}	100	16	1.27
$ClC{\equiv}C$-n-C_8H_{17}	100	19	1.34
$ClC{\equiv}C$-n-$C_{14}H_{29}$	100	9.7	1.42
$ClC{\equiv}C$-Ph	76	16	1.88
$BrC{\equiv}C$-n-C_4H_8Br	29	5.4	2.11
$MeC{\equiv}C$-n-C_5H_{11}	42	6.2	2.09
$HC{\equiv}C$-Ph	34	0.6	2.75
$HC{\equiv}C$-t-Bu	100	34	1.52
$HC{\equiv}C$-$CH(SiMe_3)$-n-C_5H_{11}	61	1.1	2.69

[a] Polymerized in toluene at 30 °C for 1 h; $[M]_0$ = 0.50 M, $[MoCl_5]$ = $[n\text{-}Bu_4Sn]$ = 20 mM, [EtOH] = 10 mM.

It is known that the organometallic cocatalysts in Table II, including not only alkyl- but also phenyl-substituted ones, generally accelerate the polymerization and enhance the monomer conversion in the absence of EtOH in the polymerization of 1-chloro-1-octyne by $MoCl_5$.[7a] In contrast, the cocatalysts other than tetraalkyltins in Table II depressed monomer conversion in the presence of EtOH. This trend is outstanding in the case where the cocatalysts employed have only phenyl groups as organic moiety and exert large steric hindrance (e.g., Ph_4Sn and Ph_3Bi). Thus, it is clear that the activity of the $MoCl_5$–cocatalyst–EtOH catalyst strongly depends on the steric effect of the cocatalyst.

Effects of oxygen-containing compounds on the polymerization of 1-chloro-1-octyne by $MoCl_5$–n-Bu_4Sn were studied (Table III). As compared with the case where they are absent, various oxygen-containing compounds maintained the quantitative monomer conversion, decreased the $\bar{M}_n$ of the polymer, and narrowed its MWD. It is noteworthy that not only compounds containing a hydroxyl or carboxyl hydrogen (alcohols and acetic acid) but also those without such active hydrogens (n-butyl acetate and acetone) are effective in giving polymers with narrow MWD. In contrast, water was ineffective in narrowing the MWD of polymer.

The narrow MWD of polymer means virtual absence of both termination and chain transfer, that is, existence of a long-lived propagating species. The formation of such a long-lived species by the addition of oxygen-containing compounds might be interpreted as follows: When oxygen-containing compounds are added to the $MoCl_5$–n-Bu_4Sn system, some chlorine atoms on the propagating species are then replaced by them. As a consequence, the formed species is to have a reduced electrophilicity, a lower activity, and a higher stability.

Polymerization of Various Acetylenes. Various substituted acetylenes are polymerizable with Mo catalysts to give high-molecular-weight polymers.[6] Hence it was examined whether the $MoCl_5$–n-Bu_4Sn–EtOH catalyst would also be effective in achieving the living polymerization of other substituted acetylenes. As seen in Table IV, 1-chloro-1-alkynes other than 1-chloro-1-octyne as well produced polymers with narrow MWDs irrespective of the length of the alkyl group ($\bar{M}_w/\bar{M}_n$ = 1.2–1.4). In contrast, the MWD of poly(1-chloro-2-phenylacetylene) was not so narrow; this might be due to the steric effect of phenyl group. Other substituted acetylenes except *tert*-butylacetylene also yielded polymers with broad MWDs. Thus, it is worth noting that the MWD of polymers greatly depends on the kind of monomers.

Conclusions

The $MoCl_5$–*n*-Bu_4Sn–EtOH catalyst system effected living polymerization of 1-chloro-1-alkynes to give polymers with narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.1–1.4). Though the present living polymerization is yet imperfect with respect to the [P*]/[Cat] ratio and the "monomer-addition" experiment, it is the first clear example of living polymerization of acetylenic monomers. Elucidation of the propagating species, improvement of the catalyst system to induce more perfect living polymerization,[12] and exploitation of other monomers that undergo living polymerization are under progress.

Acknowledgment. We thank the Ministry of Education, Science and Culture of Japan for financial support (Grant-in-Aid for Scientific Research on Priority Areas: Macromolecular Complexes, No. 62612005).

Registry No. $MoCl_5$, 10241-05-1; *n*-Bu_4Sn, 1461-25-2; EtOH, 64-17-5; Et_3SiH, 617-86-7; Ph_3SiH, 789-25-3; Ph_3Sb, 603-36-1; H_3CCO_2H, 64-19-7; H_3CCO_2-*n*-Bu, 123-86-4; H_2O, 7732-18-5; Me_4S_7, 594-27-4; 1-chloro-1-octyne (homopolymer), 100858-77-3; acetone, 67-64-1; 1-chloro-1-hexyne (homopolymer), 100858-76-2; 1-chloro-1-decyne (homopolymer), 100858-79-5; 1-chloro-1-hexadecyne (homopolymer), 108711-62-2; 1-chloro-2-phenylethyne (homopolymer), 81953-16-4; 1,6-dibromo-1-hexyne (homopolymer), 89298-41-9; 2-octyne (homopolymer), 80652-33-1; phenylethyne (homopolymer), 25038-69-1; 3,3-dimethyl-1-butyne (homopolymer), 51730-68-8; 3-trimethylsilyl-1-octyne (homopolymer), 100858-80-8.

References and Notes

(1) For a review, see: Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1.
(2) (a) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169. (b) Wallace, K. C.; Schrock, R. R. *Macromolecules* **1987**, *20*, 448. (c) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.
(3) (a) Doi, Y.; Suzuki, S.; Soga, K. *Macromolecules* **1986**, *19*, 2896. (b) Doi, Y.; Keii, T. *Adv. Polym. Sci.* **1986**, *73/74*, 201.
(4) Hadjiandreou, P.; Julemond, M.; Teyssie, P. *Macromolecules* **1984**, *17*, 2455.
(5) Krouse, S. A.; Shrock, R. R.; Cohen, R. E. *Macromolecules*, **1987**, *20*, 904.
(6) 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.
(7) (a) Masuda, T.; Yoshimura, T.; Tamura, K.; Higashimura, T. *Macromolecules* **1987**, *20*, 1734. (b) Masuda, T.; Tamura, K.; Higashimura, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1615.
(8) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, R. G. A., Asbel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, pp 499–551.
(9) (a) Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983. (b) Ivin, K. J. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: London, 1983; Vol. 1, Chapter 3.
(10) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-opening Polymerization of Cycloolefins*; Wiley-Interscience: New York, 1986.
(11) Calderon, N.; Ofstead, E. A.; Ward, J. P.; Judy, W. A.; Scott, K. W. *J. Am. Chem. Soc.* **1968**, *90*, 4133.
(12) Masuda, T.; Yoshimura, T.; Fujimori, J.; Higashimura, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1805.
(13) Ivin, K. J.; Milligan, B. D. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 269.

Synthesis of Functional Hydrocarbon Polymers with Well-Defined Molecular Structures

T. C. Chung,* M. Raate, E. Berluche, and D. N. Schulz

Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, New Jersey 08801. *Received September 23, 1987*

ABSTRACT: The paper describes the preparation of well-defined functional polymers with narrow molecular weight distributions and functional groups homogeneously distributed along the polymer chains. The chemistry involves the hydroboration of polydienes. Since both thermodynamics and kinetics are favorable for this reaction, a completely homogeneous modification is obtained. The hydroborated polymers are valuable intermediates that can be converted to a variety of functional polymers. Polyalcohol is one of the examples that will be discussed in detail in this paper. To retain the narrow molecular weight distribution, several experimental methods, including vacuum techniques, low reaction temperatures, and boric acid removal, were employed during the reaction. The resulting functional polymers have molecular weight distributions of 1.07. In the paper, we also compare the hydroboration reactivities of various unsaturated polymers. The steric effect in the hydroboration of polymers is quite similar to that of simple organic compounds.

Introduction

The area of functional polymers is becoming one of the most active in polymer science.[1-4] Many desirable properties, such as permeability, compatibility, adhesiveness, etc., can be influenced by adding specific functional groups to conventional hydrocarbon polymers.

It has been a long-time goal of synthetic polymer chemists to prepare well-defined functional polymers (including ion-containing polymers) with narrow molecular weight distributions and functional groups homogeneously distributed along the polymer chains. However, there are very few such model compounds available today. Most of the model compounds are telechelic polymers[5-8] that contain functional groups at either one or both ends of polymer chains.

This paper describes an improved method for the preparation of homogeneously functional polymers with narrow molecular weight distribution (M_w/M_n = 1.07).