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Stereospecific Living Polymerization of *tert*-Butylacetylene by Molybdenum-Based Ternary Catalyst Systems

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ABSTRACT: The polymerization of *tert*-butylacetylene (tBA) by the MoOCl$_4$–n-Bu$_4$Sn–EtOH (1:1:1) catalyst led to living *and* stereoregular polymers with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.12; cis 97%). The living nature of this polymerization was confirmed by the fact that, in toluene at 0 and -30 °C, the $\bar{M}_n$ of the polymer increases in direct proportion to monomer consumption, while the molecular weight distribution remains narrow. The cis content of the polymer was evaluated by ^{13}C NMR spectroscopy. Similar but somewhat inferior results were obtained with the MoCl$_5$–n-Bu$_4$Sn–EtOH (1:1:1) system ($\bar{M}_w/\bar{M}_n$ = 1.24; cis 90%). Besides the narrow molecular weight distribution and high cis specificity, the features of these polymerizations include large reaction rates (e.g., completed within 1 min at 0 °C) and rather low initiator efficiencies ([P*]/[Cat] ~ 2%).

Introduction

Living polymerization is one of the most useful means to control both the molecular weight and molecular weight distribution (MWD) of polymers. Recently, many living processes have been developed in not only anionic but also various types of polymerizations.[1] In metathesis polymerization, for example, several research groups including ours have succeeded in developing living polymerization systems for norbornene and its derivatives by Ti, Mo, W, and Ta carbenes,[2] substituted acetylenes by Ta and Mo carbenes,[3] 1-chloro-1-alkynes and [*o*-(trifluoromethyl)phenyl]acetylene by MoOCl$_4$ (or MoCl$_5$)–n-Bu$_4$Sn–EtOH,[4] and 1-(trimethylsilyl)-1-propyne by NbCl$_5$ in cyclohexane.[5]

The control of steric structure is another important goal in the precise synthesis of polymers. Since the steric structure of polymers greatly affects their physical properties, stereospecific polymerization has been extensively studied and many stereoregular polymers are now known. However, it still remains a very difficult and challenging subject to achieve a polymerization process that can control *simultaneously* both the MWD and steric structure of the product polymers. Thus, stereospecific *and* living polymerizations are virtually restricted to the following monomers: methyl methacrylate (anionic initiators[6] and organolanthanide complexes[7]), butadiene[8] (Ni catalysts), and an F-containing norbornadiene[9] (metathesis catalysts).

tert-Butylacetylene (tBA) produces high molecular weight polymers [number-average molecular weight ($\bar{M}_n$) > 10^5] with MoCl$_5$ and WCl$_6$.[10] The geometric structure of poly(tBA) can be determined by ^{13}C NMR spectroscopy, and *all-cis*-poly(tBA) has been obtained with MoCl$_5$ in oxygen-containing solvents.[11] There has, however, been no report on "living" poly(tBA) with a narrow MWD. In the present study, we examined the possibility of simultaneous control of the MWD and stereostructure of poly(tBA) by using Mo-based ternary catalysts that are effective in the living polymerization of other substituted acetylenes.

Experimental Section

Materials. The monomer was prepared by the addition of *tert*-butyl bromide to vinyl bromide in the presence of AlBr$_3$, followed by dehydrobromination with KOH.[12] The crude product was distilled twice from CaH$_2$ before use. The overall yield on the basis of *tert*-butyl bromide was 30%; bp 37 °C; purity 99.4% according to gas chromatography (GC). Transition-metal chlorides (MoOCl$_4$ and MoCl$_5$; Strem Chemicals; purities > 99%) and organometallic cocatalysts (n-Bu$_4$Sn, Me$_4$Sn, Ph$_4$Sn, n-Bu$_3$SnH, Et$_3$SiH, and Et$_3$Al) were commercially obtained and used without further purification. Oxygen-containing compounds such as ethanol (EtOH) were distilled before use. Polymerization solvents such as toluene were purified by the standard methods, with care being taken to remove traces of moisture and oxygen.

Procedures. Preparation of catalyst solutions and polymerization were carried out under dry nitrogen in prebaked flasks equipped with a three-way stopcock according to the following methods, unless otherwise noted. Monomer solutions were prepared by mixing tBA, n-hexane (as internal standard for GC), and toluene. Binary catalysts were prepared by mixing a transition-metal chloride, toluene, and an organometallic cocatalyst, followed by aging at 30 °C for 15 min. Ternary catalysts were obtained by further adding an oxygen-containing compound to the binary catalyst solutions and aging at 0 °C for an additional 15 min.

Polymerizations were initiated by adding a monomer solution to a catalyst solution and quenched with a mixture (2 mL) of methanol and toluene (1:4 volume ratio). Monomer conversion was determined by GC. The quenched polymerization solutions were diluted with toluene (20 mL) and poured into methanol (1 L). The precipitated polymers were filtered off, washed with methanol, and dried to constant weight under vacuum. Polymer yields were determined by gravimetry.

Polymer Characterization. ^{13}C NMR spectra of the polymers were measured in CDCl$_3$ at room temperature on a JEOL GSX-270 spectrometer. Chemical shifts were determined with tetramethylsilane as the internal standard. The MWD curves of the polymers were observed by gel permeation chromatography (GPC) using a Jasco Trirotar liquid chromatograph (columns, Shodex A804, A806, and A807; eluent, CHCl$_3$). The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$, respectively) were calculated by use of a polystyrene calibration.

Results and Discussion

Living Polymerization of *tert*-Butylacetylene. Polymerization of tBA was performed in toluene at 0 °C by use of various Mo catalysts, including MoOCl$_4$, MoOCl$_4$–n-Bu$_4$Sn (1:1), MoOCl$_4$–n-Bu$_4$Sn–EtOH (1:1:1), MoCl$_5$, MoCl$_5$–n-Bu$_4$Sn (1:1), and MoCl$_5$–n-Bu$_4$Sn–EtOH (1:1:1). With all these catalysts, the monomer was completely consumed within 1 min, and the polymer was obtained quantitatively. Under the standard polymerization conditions ([M]$_0$ = 0.50 M, [Cat] = 20 mM), MoOCl$_4$ and MoCl$_5$ alone produced polymers partly insoluble in CHCl$_3$, probably owing to the very high molecular weight. In order to obtain a soluble polymer with a lower molecular weight, the MoOCl$_4$-catalyzed polymerization was carried out at

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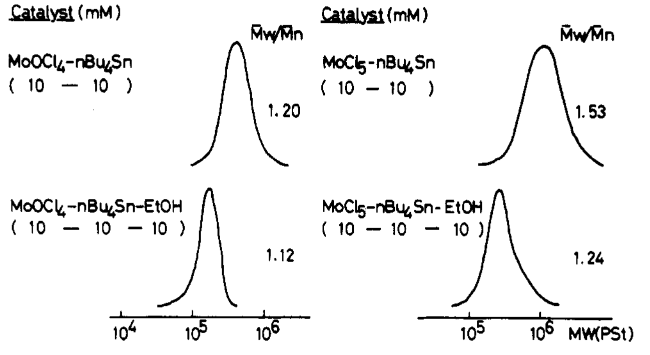


Figure 1. MWD curves of poly(tBA)s obtained with Mo catalysts (polymerized in toluene at 0 °C for 10 min; $[M]_0 = 0.50$ M; conversions ~100%).

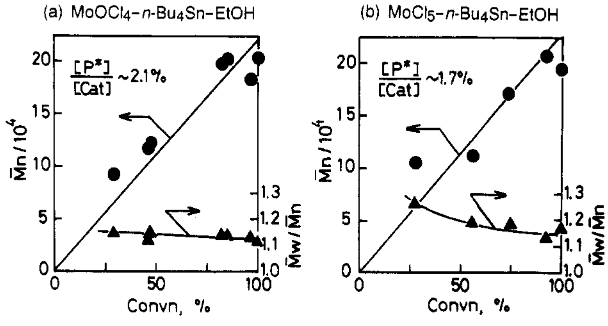


Figure 2. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(tBA) obtained with $MoOCl_4$ (or $MoCl_5$)-n-Bu_4Sn-EtOH (1:1:1), as a function of monomer conversion (polymerized in toluene at -30 °C; $[M]_0 = 0.50$ M, [Mo] = 10 mM).

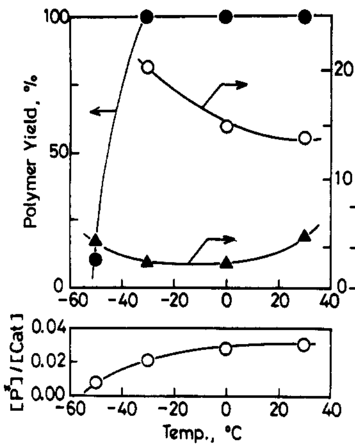


Figure 3. Effect of temperature on the polymerization of tBA by $MoOCl_4$-n-Bu_4Sn-EtOH (1:1:1) (polymerized in toluene for 10 min; $[M]_0 = 0.50$ M, $[MoOCl_4] = 10$ mM; conversions ~100%).

Table 1. Effects of Cocatalysts on the Polymerization of tBA by $MoOCl_4$-Cocatalyst-EtOH (1:1:1)[a]

	polymer				
cocatalyst	time, h	yield, %	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	[P*]/[Cat]
n-Bu_4Sn	1/6	100	149	1.12	0.028
Me_4Sn	1/6	100	b		
Ph_4Sn	24	61	b		
n-Bu_3SnH	24	0	b		
Et_3SiH	24	96	b		
Et_3Al	24	100	b		

[a] Polymerized in toluene at 0 °C; $[M]_0 = 0.50$ M, [Cat] = 10 mM.
[b] Partly insoluble in $CHCl_3$.

a lower monomer/catalyst ratio ($[M]_0 = 0.25$ M, [Cat] = 30 mM). In fact, the formed polymer was totally soluble in $CHCl_3$, whose $\bar{M}_n$ was 4.48×10^4 with a broad MWD ($\bar{M}_w/\bar{M}_n$ 2.29).

Figure 1 illustrates the MWD curves of poly(tBA)s obtained with the Mo-based binary and ternary catalysts. The binary catalysts ($MoOCl_4$-n-Bu_4Sn and $MoCl_5$-n-Bu_4Sn) yielded polymers having fairly narrow MWD's ($\bar{M}_w/\bar{M}_n$1.20 and 1.53, respectively). Further addition of ethanol as a third catalyst component decreased the $\bar{M}_w/\bar{M}_n$ to 1.12 ($MoOCl_4$-n-Bu_4Sn-EtOH) and 1.24 ($MoCl_5$-n-Bu_4Sn-EtOH). Thus, the $MoOCl_4$- and $MoCl_5$-based ternary catalysts prove to afford poly(tBA)s with the narrowest MWD's.

The relationship between monomer conversion and $\bar{M}_n$ was examined for the polymerizations with $MoOCl_4$-n-Bu_4Sn-EtOH and $MoCl_5$-n-Bu_4Sn-EtOH. Since the polymerizations were too fast at 0 °C to monitor (completed within 1 min), the time course of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ was followed at -30 °C (completion of reaction needed ca. 10 min). As seen in Figure 2, the $\bar{M}_n$'s of the polymers formed with both catalysts increase in direct proportion to monomer consumption, while the MWD's stay narrow. These results lead to a conclusion that the polymerizations are living. The $MoOCl_4$-based catalyst is superior to the $MoCl_5$-based counterpart, as judged from the $\bar{M}_w/\bar{M}_n$ profiles.

The initiator efficiency ([P*]/[Cat]) was calculated from eq 1:

$$[P^*]/[Cat] = [M]_{consumed}/(DP_n \times [Cat]) \qquad (1)$$

where DP_n is the number-average degree of polymerization determined by GPC. The initiator efficiencies for the $MoOCl_4$- and $MoCl_5$-based ternary catalysts at -30 °C were 2.1% and 1.7%, respectively. These values are smaller than those (5–10%) for the living polymerizations of 1-chloro-1-octyne and [o-(trifluoromethyl)phenyl]acetylene at +30 °C.[4] The lower efficiency for tBA may be attributed to its high reactivity and the low polymerization temperature.

Figure 3 shows the effect of polymerization temperature. The polymerizations were all run for 10 min. Polymers were obtained quantitatively at -30 °C and above. The MWD is narrow ($\bar{M}_w/\bar{M}_n$ ~ 1.1) at -30 and 0 °C but becomes broader at 30 °C ($\bar{M}_w/\bar{M}_n > 1.2$). Though the [P*]/[Cat] tends to increase with raising temperature, it remains as low as 3% even at +30 °C. It is noted that the living polymerization of tBA proceeds successfully at -30 and 0 °C, while those of 1-chloro-1-octyne and [o-(trifluoromethyl)phenyl]acetylene proceed at 0 and +30 °C, which is attributable to the high reactivity of tBA.

Effects of organometallic cocatalysts were examined with the catalyst system, $MoOCl_4$-cocatalyst-EtOH (Table 1). The polymerization using n-Bu_4Sn as cocatalyst was completed in ca. 1 min, and a living polymer with an $\bar{M}_w/\bar{M}_n$ of 1.12 was obtained. The polymer obtained with Me_4Sn as cocatalyst was partly insoluble in $CHCl_3$, although the polymerization proceeded at a rate similar to that with n-Bu_4Sn. In contrast, the polymerizations using other cocatalysts, such as Ph_4Sn, Et_3SiH, and Et_3Al, were sluggish and resulted in polymers partly insoluble in $CHCl_3$. It is interesting to note here that the polymerizations of tBA by the binary $MoOCl_4$-cocatalyst systems are very rapid irrespective of the kind of cocatalysts. These results suggest that, in the presence of ethanol, the mechanism of metal carbene formation and/or the activity of the resulting metal carbene is substantially different between tetraalkyltins and other types of organometallic cocatalysts.

Effects of various oxygen-containing compounds as third catalyst components of the $MoOCl_4$-n-Bu_4Sn-O-compound system are shown in Table 2. The $\bar{M}_w/\bar{M}_n$ (1.21)

Table 2. Effects of Oxygen-Containing Compounds (O-compd) on the Polymerization of tBA by $MoOCl_4$-n-Bu_4Sn-EtOH (1:1:1)[a]

	polymer			
O-compd	yield, %	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	[P*]/[Cat]
none	100	183	1.21	0.022
EtOH	100	149	1.12	0.028
PhOH	100	185	1.17	0.022
CH_3COOH	100	306	1.30	0.013
CH_3COO-n-Bu	100	176	1.27	0.023
acetone	100	192	1.66	0.021

[a] Polymerized in toluene at 0 °C for 10 min; $[M]_0 = 0.50$ M, [Cat] = 10 mM.

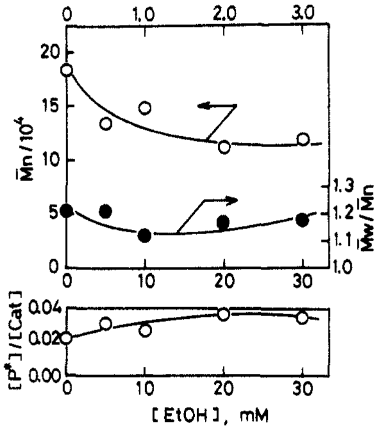
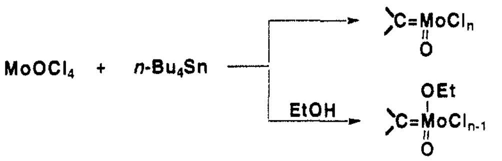


Figure 4. Effect of ethanol concentration on the polymerization of tBA by $MoOCl_4$-n-Bu_4Sn-EtOH (polymerized in toluene at 0 °C for 10 min; $[M]_0 = 0.50$ M, $[MoOCl_4] = [n\text{-}Bu_4Sn] = 10$ mM; conversions ~100%).

is fairly small even with the binary $MoOCl_4$-n-Bu_4Sn system. However, addition of ethanol as a third component made the ratio even smaller (=1.12). Phenol hardly affected $\bar{M}_w/\bar{M}_n$, while other oxygen-containing compounds gave adverse effects upon $\bar{M}_w/\bar{M}_n$. As has been previously proposed,[4c] ethanol is considered to replace a chlorine ligand of the metal carbene with an ethoxy group to give a less active but more stable propagating species (eq 2).



$$MoOCl_4 + n\text{-}Bu_4Sn \longrightarrow \begin{cases} \rangle C{=}\underset{\underset{O}{\|}}{Mo}Cl_n \\ \xrightarrow{EtOH} \rangle C{=}\overset{OEt}{\underset{\underset{O}{\|}}{Mo}}Cl_{n-1} \end{cases} \quad (2)$$

Figure 4 depicts the effect of ethanol concentration for the polymerization with $MoOCl_4$-n-Bu_4Sn-EtOH. The addition of ethanol equivalent to $MoOCl_4$ achieved the smallest $\bar{M}_w/\bar{M}_n$ value (1.12). The initiator efficiency tended to increase with increasing the amount of ethanol to reach 3.0% at [EtOH] = 20 mM (or 2 equiv to $MoOCl_4$). This shows that only a part of the added ethanol interacts with the propagating species.

The effects of various polymerization solvents were examined (Table 3). The $\bar{M}_w/\bar{M}_n$ of polymer was 1.12 in toluene, while it was larger in halogenated solvents (chlorobenzene and CCl_4). Though polymerizations proceeded rapidly also in anisole and heptane, the MWD's were broad. These are attributable to the insolubility of poly(tBA) in anisole and the poor solubility of $MoOCl_4$ in heptane. Eventually, toluene has turned out to be the most suitable solvent to achieve the present living polymerization.

Table 3. Effects of Solvents on the Polymerization of tBA by $MoOCl_4$-n-Bu_4Sn-EtOH (1:1:1)[a]

	polymer			
solvent	yield, %	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	[P*]/[Cat]
toluene	100	149	1.12	0.028
PhCl	100	128	1.27	0.031
CCl_4	100	122	1.34	0.034
heptane	100	262	2.22	0.016
PhOMe	100	186	3.29	0.022

[a] Polymerized at 0 °C for 10 min; $[M]_0 = 0.50$ M, [Cat] = 10 mM.

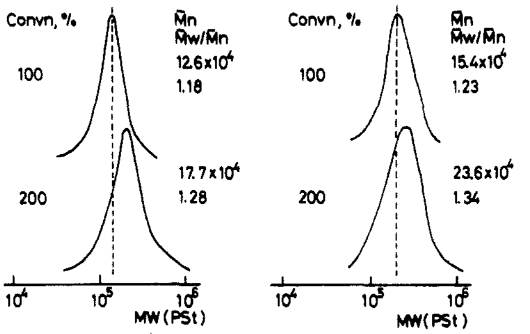
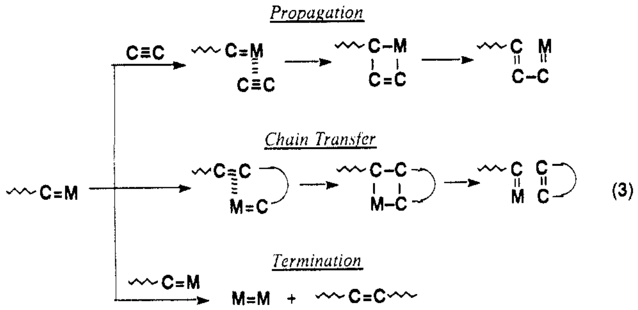


Figure 5. MWD curves of poly(tBA)s obtained with $MoOCl_4$ (or $MoCl_5$)-n-Bu_4Sn-EtOH (1:1:1) in the "monomer addition experiment" (polymerized in toluene at 0 °C for 1 min each; $[M]_0 = [M]_{added} = 0.25$ M, [Mo] = 10 mM).

The so-called "monomer addition experiment" was carried out to further examine the living nature of the polymerization of tBA by $MoOCl_4$- and $MoCl_5$-based ternary catalysts (Figure 5). After the first fed monomer ($[M]_0 = 0.25$ M) had been completely consumed, a new monomer feed ($[M]_{added} = 0.25$ M) was supplied. The second added monomer also polymerized rapidly to completion with both catalysts. However, the $\bar{M}_n$'s of the polymers did not double, and the MWD's became somewhat broader, which implies some deactivation of the propagating species during the second-stage polymerization. Thus, the propagating species formed from tBA is less stable than those formed from 1-chloro-1-octyne and [o-(trifluoromethyl)phenyl]acetylene for which the monomer addition experiments were very successful.[4] However, no additional molecular peak is seen and the initiator efficiencies remain virtually constant, both of which indicate that the propagating species are formed only at the initial stage.

A plausible polymerization mechanism is shown in eq 3. The polymerization of tBA and related alkynes is thought to proceed via the following three steps: coordination of a monomer to a metal carbene, formation of a metallacyclobutene by their cycloaddition, and the subsequent ring scission of the metallacycle. Sterically crowded monomers like tBA appear to prompt the ring scission owing to steric effects, which might be responsible for their high reactivity in polymerization. Chain transfer might occur through a metathesis reaction between the propagating end and a double bond of the polymer chain either intramolecularly (so called "back-biting" reaction)



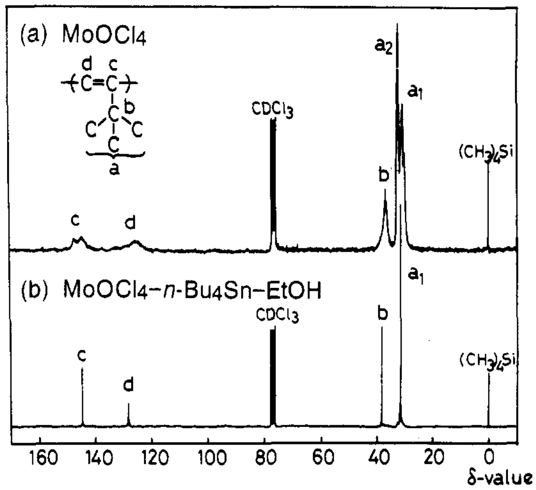


Figure 6. ^{13}C NMR spectra of poly(tBA)s obtained with (a) $MoOCl_4$ and (b) $MoOCl_4$–n-Bu_4Sn–EtOH (1:1:1) (polymerized in toluene at 0 °C for 10 min; $[M]_0 = 0.50$ M, $[MoOCl_4] = 10$ mM; conversions ~100%).

or intermolecularly. Use of a sterically crowded monomer will help depress such a chain-transfer process. Possible termination reactions include a bimolecular coupling of the propagating species and/or its reaction with impurities present in the systems. As discussed already, addition of ethanol as a third catalyst component may form an ethoxy-containing stable propagating species (eq 2), which is less prone to termination reactions. These requirements are apparently satisfied in the present living polymerization of tBA. The initiator efficiency of the present polymerization is rather low but higher than that (<1%) of the polymerization of norbornene by WCl_6–Me_4Sn.[13] In general, it appears difficult to generate metal carbenes in high yield from metal chloride-based catalysts.

Stereostructure of Poly(*tert*-butylacetylene). Since it was found that tBA polymerizes in a living fashion with the Mo-based ternary catalysts, we then became interested in controlling the stereostructure (geometric structure) of the living poly(tBA). Fortunately, the geometric structure of poly(tBA) can be easily determined by ^{13}C NMR.[11] Figure 6 compares ^{13}C NMR spectra of two poly(tBA) samples obtained in toluene at 0 °C, one formed with $MoOCl_4$–n-Bu_4Sn–EtOH having a narrow MWD [a living poly(tBA)] and the other formed with $MoOCl_4$ alone. In the spectrum of the poly(tBA) formed with $MoOCl_4$ alone, the signal due to the methyl carbons of the *tert*-butyl group splits into two peaks at 31.2 and 32.4 ppm. These peaks are attributable to cis and trans structures, respectively.[11a] In addition, the signals of other carbons (peaks b–d) are rather broad. All these features indicate an irregular geometric structure of the sample. On the other hand, the living poly(tBA), obtained with $MoOCl_4$–n-Bu_4Sn–EtOH, exhibits a single, very sharp methyl peak at 31.2 ppm assignable to the cis structure. The signals of the other carbons are also very sharp. The cis content of the living poly(tBA) was determined as 91% on the basis of the peak areas. Thus, it is quite interesting that the living poly(tBA) obtained with $MoOCl_4$–n-Bu_4Sn–EtOH at 0 °C shows a fairly high stereoregularity.

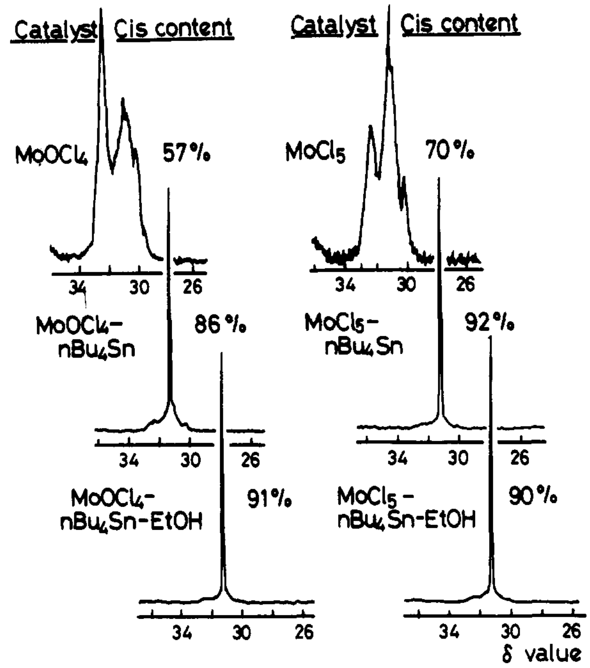


Figure 7. Effect of catalyst components on the cis content of poly(tBA) (polymerized in toluene at 0 °C for 10 min; $[M]_0 =$ 0.50 M, $[Mo] = [n\text{-}Bu_4Sn] = [EtOH] = 10$ mM; conversions ~100%).

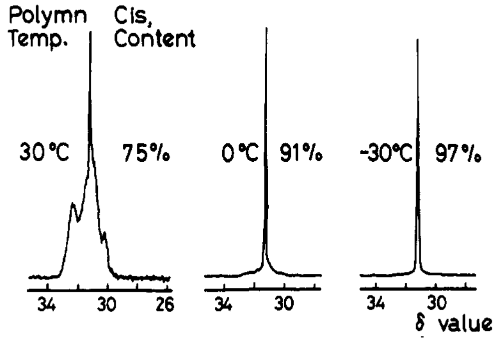


Figure 8. Effect of polymerization temperature on the cis content of poly(tBA) obtained with $MoOCl_4$–n-Bu_4Sn–EtOH (1:1:1) (polymerized in toluene for 10 min; $[M]_0 = 0.50$ M, $[MoOCl_4] = 10$ mM; conversions ~100%).

In order to clarify which of the three catalyst components mainly controls the stereostructure of poly(tBA), we investigated the stereostructure of poly(tBA) obtained with various $MoOCl_4$- and $MoCl_5$-based catalysts (Figure 7). The cis contents with $MoOCl_4$ and $MoCl_5$ alone were rather low (57 and 70%, respectively). When n-Bu_4Sn was employed as cocatalyst, the cis contents considerably increased to as high as ca. 90% with both $MoOCl_4$ and $MoCl_5$. Ethanol as the third catalyst component affected the cis content only slightly. These results lead to a conclusion that n-Bu_4Sn as cocatalyst is the major factor governing the stereostructure of poly(tBA).

The effect of the polymerization temperature on the stereostructure of the polymer obtained with $MoOCl_4$–n-Bu_4Sn–EtOH was examined (Figure 8). While the cis content of poly(tBA) is no more than 75% at +30 °C, it sharply increases with lowering the temperature to reach 97% at −30 °C. Thus very importantly, the poly(tBA) formed with $MoOCl_4$–n-Bu_4Sn–EtOH at −30 °C is a stereoregular *and* living polymer with 97% cis and an $\bar{M}_w/\bar{M}_n$ of 1.12.

In conclusion, stereospecific living polymerization of tBA was achieved by using the $MoOCl_4$–n-Bu_4Sn–EtOH ternary catalyst system (cis 97%; $\bar{M}_w/\bar{M}_n = 1.12$). As mentioned in the Introduction, stereospecific living polymerizations are rare, even when one considers all the known polymerization mechanisms. This work presents a new example of such doubly controlled polymerizations, which is also the first example for substituted acetylenes.

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