Stereospecific Polymerization of *tert*-Butylacetylene by Molybdenum Catalysts. Effect of Acid-Catalyzed Geometric Isomerization

Toshio Masuda,* Hiroshi Izumikawa, Yoshihiko Misumi, and Toshinobu Higashimura

Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan

Received August 14, 1995; Revised Manuscript Received November 16, 1995[⊗]

ABSTRACT: Stereospecificity of the polymerization of *tert*-butylacetylene by Mo-based catalysts was investigated. The polymer obtained by the $MoOCl_4$−*n*-Bu_4Sn system just after complete monomer consumption had an all-cis structure. However, the stereoregularity decreased when the polymerization was allowed to stand further. These findings indicate that, though the propagation reaction proceeds stereospecifically, the geometric isomerization of polymer lowers stereoregularity. This isomerization was catalyzed by several acids as well as by polymerization catalysts and, hence, is an acid-catalyzed reaction. Highly stereoregular polymer could be obtained by accelerating polymerization (by use of cocatalysts) and/or by decelerating isomerization (by use of cocatalysts, poor solvents of the polymer, or the less acidic $Mo(CO)_6$-based catalyst and by polymerization at low temperatures).

Introduction

Polyacetylenes have been attracting much attention for their salient features such as high electrical conductivity and gas permeability.[1] Since the physical properties of polymers are greatly affected by their steric structure, it is an important subject to control the steric structure of polymers. To our knowledge, however, stereospecific polymerizations of acetylenes have been restricted to the following systems: acetylene/Ti(O-*n*-Bu)$_4$−Et_3Al catalyst,[2] phenylacetylenes/Rh catalysts,[3] alkyl propiolates/Rh catalysts,[4] *tert*-butylacetylene (tBA)/Mo catalysts/polar solvents.[5]

We recently achieved a living and stereospecific polymerization of tBA by use of the $MoOCl_4$−*n*-Bu_4Sn−EtOH (1:1:1) catalyst;[6] the mechanism of generating the stereospecificity was, however, not clear. The steric structure of poly(tBA) can be readily determined by ^{13}C NMR. Accordingly, analysis of the steric structure of poly(tBA) obtained under various conditions should provide useful information on the stereospecific polymerization of tBA.

In the present study, we investigated factors controlling the steric structure of polymer in the polymerization of tBA by molybdenum catalysts. Studies on the time dependence of polymerization revealed that an all-cis polymer was formed in the early stage, followed by geometric isomerization of the polymer. This isomerization was catalyzed by a variety of acids including polymerization catalysts. Thus this study has clarified the following: (i) the propagation reaction proceeds stereospecifically even in the polymerization system that was considered nonstereospecific before, and (ii) the subsequent geometric isomerization of polymer greatly affects the steric structure.

Experimental Section

Materials. The monomer was prepared by the $AlBr_3$-catalyzed addition of *tert*-butyl bromide to vinyl bromide, followed by dehydrobromination with KOH.[7] 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 99.5% according to gas chromatography (GC). Transition metal chlorides ($MoOCl_4$, $MoCl_5$, and WCl_6; Strem Chemicals; purities > 99%), Ph_4Sn, $SnCl_4$, I_2, $EtAlCl_2$, and CF_3SO_3H were commercially obtained and used without further purification. *n*-Bu_4Sn, EtOH, and THF were distilled before use. Polymerization solvents such as toluene were purified by the standard methods, care being taken to remove traces of moisture and oxygen.

Procedures. Preparation of catalyst solutions and polymerization were carried out according to the procedures reported in the preceding paper.[6] Polymerizations were initiated by adding a monomer solution to a catalyst solution and quenched with ammoniacal *n*-BuOH. Monomer conversions were determined by GC. The quenched polymerization solutions were poured into a large amount of methanol. The precipitated polymers were filtered off and dried to constant weight in vacuo. Polymer yields were determined by gravimetry.

The poly(tBA) used for the isomerization reaction was prepared by the polymerization in toluene at 0 °C for 1 min using $MoOCl_4$−*n*-Bu_4Sn−EtOH (1:1:1) catalyst ($[M]_0$ = 0.50 M, $[MoOCl_4]$ = 10 mM). The polymer was isolated by precipitation in methanol and dried in vacuo. It was further dissolved in benzene at 80 °C and freeze-dried at 0 °C. Acid-catalyzed isomerization reactions were carried out under nitrogen in toluene at 0 °C under stirring. After quenching the reaction with ammoniacal methanol, the mixture was poured into methanol and the precipitated polymer was filtered and dried in vacuo.

Polymer Characterization. The ^{13}C NMR spectra of poly(tBA)s were measured in $CDCl_3$ at room temperature on a JEOL GSX-270 spectrometer (68 MHz for ^{13}C). Chemical shifts were determined with tetramethylsilane as the internal standard. The cis contents of the polymers were calculated according to the following equation for convenience:

$$\text{cis content (\%)} = 100 \times H_a/(H_a + H_b + H_c) \qquad (1)$$

where H_a, H_b, and H_c are the heights of the signals at 31.2, 32.4, and 30.2 ppm, respectively. The molecular weight distribution curves of the polymers were observed by gel permeation chromatography (GPC) using a JASCO Trirotar liquid chromatograph (columns Shodex K803, K804, and K805; eluent $CHCl_3$). The number- and weight-average molecular weights (M_n and M_w, respectively) were calculated by use of a polystyrene calibration.

Results and Discussion

Stereospecific Polymerization of tBA by Mo-Based Catalysts and Isomerization of the Polymer. Figure 1 illustrates ^{13}C NMR spectra of the

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

0024-9297/96/2229-1167$12.00/0

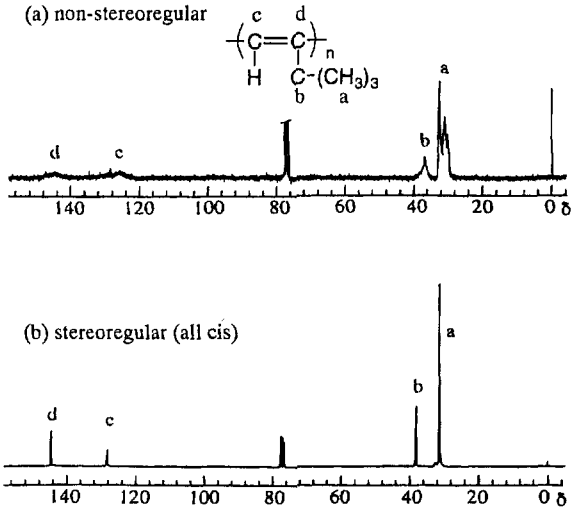


Figure 1. ^{13}C NMR spectra of poly(tBA)s obtained with (a) $MoOCl_4$ and (b) $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:1) (polymerized in toluene at 0 °C for 10 min; $[M]_0$ = 0.50 M, $[MoOCl_4]$ = 10 mM; conversions ~100%).

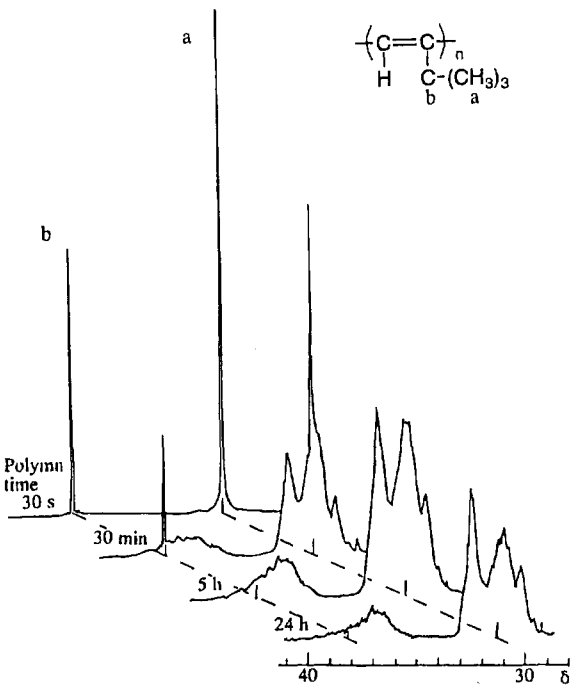


Figure 2. Effect of polymerization time on the ^{13}C NMR spectrum (aliphatic region) of poly(tBA) obtained with $MoOCl_4$–*n*-Bu_4Sn (1:1) (polymerized in toluene at 0 °C; $[M]_0$ = 0.20 M, $[MoOCl_4]$ = 20 mM; conversions ~100%).

poly(tBA)s obtained with $MoOCl_4$ alone and $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:1) in toluene at 0 °C for 10 min. The upper spectrum (catalyst: $MoOCl_4$) exhibits a split signal due to the methyl carbons of the *tert*-butyl group and broad signals due to the olefin and methine carbons; this means that the contents of cis and trans structures are comparable and that the stereoregularity of the polymer is low. In contrast, the lower spectrum (catalyst: $MoOCl_4$–*n*-Bu_4Sn–EtOH) shows a single and sharp signal assigned to the methyl carbons of the *tert*-butyl group, and the other signals are also single and sharp; this polymer was concluded to have an all-cis structure on the basis of molecular modelings and CNDO calculations.[8] Thus, which of $MoOCl_4$ and $MoOCl_4$–*n*-Bu_4Sn–EtOH is used as catalyst generates a remarkable difference in the structure of the formed

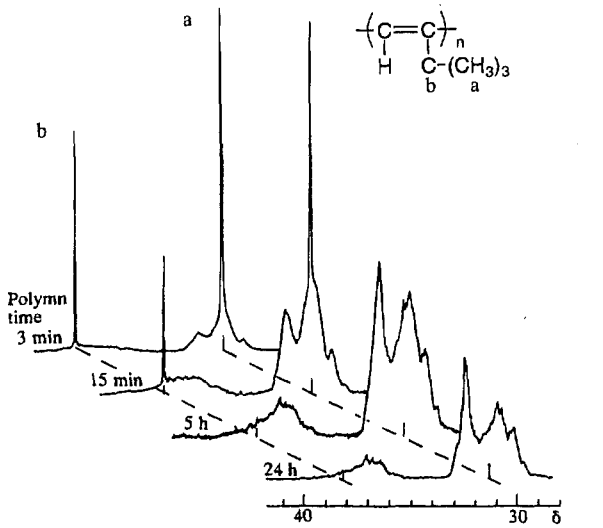


Figure 3. Effect of polymerization time on the ^{13}C NMR spectrum (aliphatic region) of poly(tBA) obtained with $MoCl_5$ (polymerized in toluene/anisole (1:1) at 30 °C; $[M]_0$ = 0.20 M, $[MoCl_5]$ = 20 mM).

polymers. This prompted us to study the structure of the polymer obtained with $MoOCl_4$–*n*-Bu_4Sn, a binary catalyst.

The effect of polymerization time on the steric structure of the poly(tBA) obtained with $MoOCl_4$–*n*-Bu_4Sn (1:1) in toluene was investigated (Figure 2). The polymerization system was homogeneous, and the polymer was soluble in toluene and $CHCl_3$. The monomer conversion and the polymer yield reached 99.7 and 95%, respectively, after polymerization for 30 s. The polymer showed very sharp signals for the *tert*-butyl group in the ^{13}C NMR spectrum, indicating high stereoregularity (almost all-cis). However, as the polymerization time elapsed, the cis content of the polymer lowered. Eventually, a nonstereoregular polymer with a cis content of 30% formed after polymerization for 24 h.

Figure 3 illustrates the polymerization-time dependence of the ^{13}C NMR spectrum of the poly(tBA) obtained with $MoCl_5$ in toluene/anisole (1:1) solution. The polymer was not completely soluble in the polymerization system, but soluble in toluene and $CHCl_3$. After polymerization for 3 min, the monomer conversion reached 93%, and the polymer possessed a very high cis content. However, like the case of Figure 2, the cis content decreased when the system was left further.

These results clearly show that these polymerizations are stereospecific (all-cis) but that the stereoregularity of the polymer remarkably decreases as a result of geometric isomerization of the polymer.

Katz and Lee have proposed a general mechanism by which the geometric structure of substituted polyacetylenes is determined in the metathesis mechanism.[9] It is not clear yet which of metal carbenes **1** and **2** is formed in tBA polymerization (Scheme 1). Hence two detailed mechanisms are possible for the selective formation of the cis structure (Scheme 1): (a) in the case where the *tert*-butyl group is in the α-position of the intermediary alkylidene complex, the steric repulsion in the metallacyclobutene between the *tert*-butyl group in the penultimate unit and the central metal results in the cis structure, and (b) in the case where hydrogen is in the α-position of the intermediary alkylidene complex, the steric repulsion between the *tert*-butyl group in the terminal unit and the polymer chain leads to the cis structure.

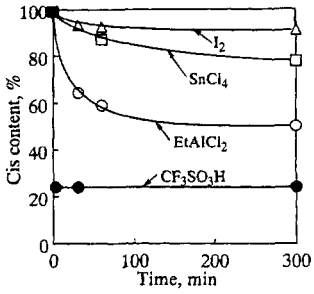
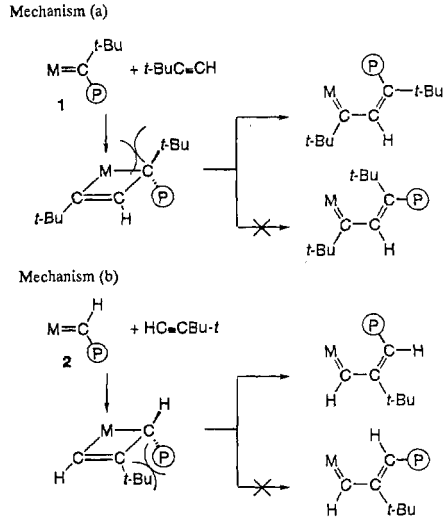


Figure 4. Isomerization of poly(tBA) by I_2, $SnCl_4$, CF_3SO_3H, and $EtAlCl_2$ (in toluene, 0 °C, [C=C] = 0.20 M, [catalyst] = 20 mM).

Scheme 1



Mechanism of the Geometric Isomerization of Poly(tBA): Acid Catalysis. To gain knowledge about the mechanism of the geometric isomerization of poly(tBA), we investigated isomerization of an all-cis polymer obtained with $MoOCl_4$–*n*-Bu_4Sn–EtOH. Since it was presumed that the isomerization would proceed through acid catalysis by the remaining metal chlorides, the polymer was allowed to react with catalytic amounts of various acids. The reactions were carried out in toluene at 0 °C. The stronger the Lewis acidity of the acid, the more bluish the system became; this blue color disappeared when ammoniacal methanol was added. As seen from Figure 4, the cis content of the polymer decreased in the presence of any of I_2, $SnCl_4$, $EtAlCl_2$, and CF_3SO_3H. The isomerization rate was in the order CF_3SO_3H > $EtAlCl_2$ > $SnCl_4$ > I_2. In particular, the cis content reached an equilibrium within 3 min in the presence of CF_3SO_3H.

The finding that the isomerization is caused by various acids and proceeds faster with stronger acids leads to a conclusion that the isomerization of poly(tBA) is an acid catalysis.

Figure 5 shows results for the isomerization of polymer by polymerization catalysts. When $MoOCl_4$ alone was used, fast isomerization occurred. Addition of cocatalysts (organotins) lowered the rate of the isomerization. This is explained in terms that the ligand exchange between a metal chloride and a cocatalyst lowers the acidity of the metal chloride.

The isomerization was accompanied by a molecular weight decrease (degradation) of the polymer. Figure 6a illustrates the time dependence of the GPC curve in the isomerization by $MoOCl_4$. After broadening of the

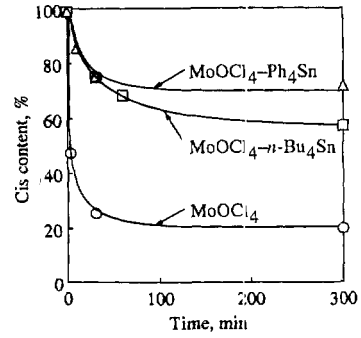


Figure 5. Isomerization of poly(tBA) by $MoOCl_4$-based catalysts (in toluene, 0 °C, [C=C] = 0.20 M, [$MoOCl_4$] = [Sn] = 20 mM).

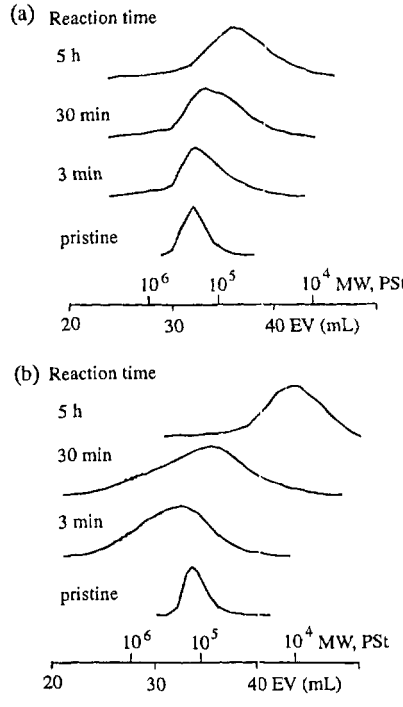
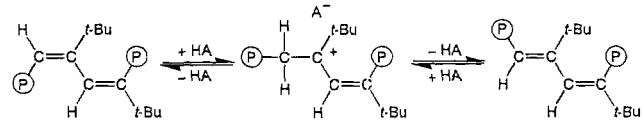


Figure 6. Effect of isomerization time on the GPC curve of poly(tBA)s treated with (a) $MoOCl_4$ and (b) CF_3SO_3H (in toluene, 0 °C, [C=C] = 0.20 M, [$MoOCl_4$] = [CF_3SO_3H] = 20 mM).

Scheme 2



GPC peak, it shifted to the low molecular weight side. Whereas the isomerization reached an equilibrium within 30 min (Figure 5), the degradation proceeded further. Degradation was also observed in the isomerization by CF_3SO_3H (Figure 6b), while it scarcely occurred in the isomerization by $MoOCl_4$–*n*-Bu_4Sn (1:1). The molecular weight decreased approximately to one-tenth that of the starting polymer after 5 h with CF_3SO_3H. These results indicate that the degradation of polymer is also an acid-catalyzed reaction.

Based on the above-described results, we propose the isomerization mechanism including an allyl cation intermediate, as shown in Scheme 2. That is to say, the isomerization proceeds via addition and subsequent elimination of proton to the main-chain double bonds. The geometric structure of the main chain is governed

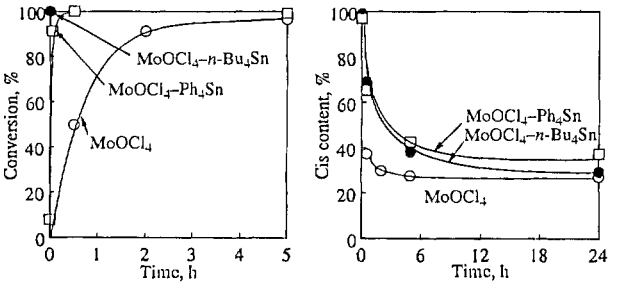


Figure 7. Polymerization of tBA by $MoOCl_4$-based catalysts (in toluene, 0 °C, $[M]_0 = 0.20$ M, $[MoOCl_4] = [Sn] = 20$ mM).

by the direction of elimination of one of the two methylene protons adjacent to the allyl cation formed by addition of proton to a double bond of the main chain. For the above-mentioned polymer degradation, we assume the mechanism that an allyl cation disproportionates into a vinyl cation and a vinyl terminal.

It has been known that isomerization of polyalkenamers such as polynorbornene is caused by secondary metathesis in the polymerization system.[10] However, self-metathesis has not been known for tri- or tetrasubstituted ethylenes.[11] Substituted polyacetylenes can be regarded as sequences of tri- or tetrasubstituted ethylenes, and further, the double bond of the main chain is surrounded by bulky substituents. Hence the secondary metathesis is unlikely.

Effects of Polymerization Conditions on the Isomerization of Poly(tBA). The above-stated results manifest that the stereoregularity of poly(tBA) is governed by not only the stereospecificity of the propagation reaction but also the acid-catalyzed geometric isomerization of the polymer. It is interesting to clarify how the rate of isomerization is affected by the polymerization conditions. Therefore we examined time profiles of the monomer conversion and the cis content of polymer in the polymerization of tBA by molybdenum catalysts under various conditions.

Effects of cocatalysts were examined (Figure 7). When $MoOCl_4$ alone was used, i.e., no cocatalyst was employed, the polymerization proceeded rather slowly. In contrast, the polymerizations using n-Bu_4Sn and Ph_4Sn as cocatalysts proceeded very rapidly (e.g., the polymerization with n-Bu_4Sn was complete within 30 s). Regarding geometric structure, a polymer with low stereoregularity (cis content 30–40%) was obtained with $MoOCl_4$ alone. In contrast, when n-Bu_4Sn was employed as cocatalyst, almost 100% of cis content was observed at the completion of polymerization. After then, however, the cis content gradually decreased. In the case of Ph_4Sn, the cis content was again almost 100% in the early stage of polymerization, but it became 70% at the completion of polymerization. In every case, the cis content eventually reached an equilibrium at 30–40%. Since the isomerization of polymer with $MoOCl_4$ alone is very fast, the results for $MoOCl_4$ catalyst do not necessarily mean low stereospecificity of the propagation reaction. In other words, propagation may be essentially stereospecific in all the cases, and the apparent stereospecificity depends on the relative rates of polymerization and isomerization which are influenced by the addition of cocatalysts. More specifically, a stereoregular poly(tBA) can be obtained when polymerization is sufficiently faster than isomerization.

Figure 8 shows the variation of cis content in the $MoOCl_4$–n-Bu_4Sn-catalyzed polymerization in several solvents. Isomerization proceeded in good solvents of

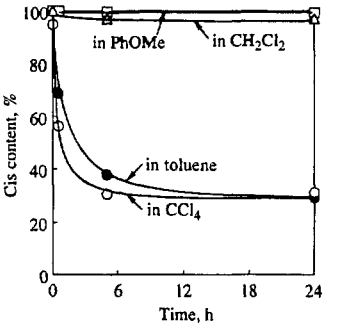


Figure 8. Effect of polymerization solvents on the cis content of poly(tBA) obtained with $MoOCl_4$–n-Bu_4Sn (1:1) (0 °C, $[M]_0 = 0.20$ M, $[MoOCl_4] = 20$ mM).

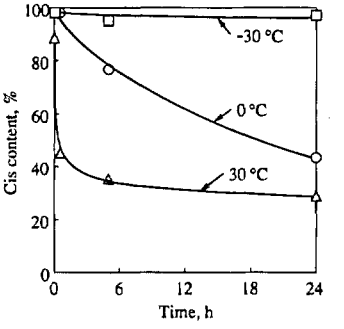


Figure 9. Effect of polymerization temperature on the cis content of poly(tBA) obtained with $MoOCl_4$–n-Bu_4Sn–EtOH (1:1:1) (in toluene, $[M]_0 = 0.20$ M, $[MoOCl_4] = 20$ mM).

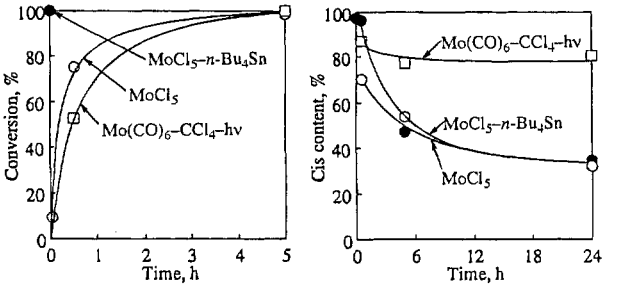


Figure 10. Polymerization of tBA by $MoCl_5$- and $Mo(CO)_6$-based catalysts (at 0 °C, $[M]_0 = 0.20$ M; ($MoCl_5$-based catalysts) in toluene, $[MoCl_5] = 20$ mM; ($Mo(CO)_6$-based catalyst) in CCl_4, $[Mo(CO)_6] = 10$ mM).

the polymer such as toluene and CCl_4, whereas it hardly occurred in nonsolvents like anisole and CH_2Cl_2. This suggests that the polymer should stay dissolved in a solvent so that the acid-catalyzed isomerization may take place.

Temperature dependence of the polymerization is shown in Figure 9. The lower the polymerization temperature, the slower the isomerization, and the isomerization scarcely proceeded at −30 °C. It was thus confirmed that it is effective to perform the polymerization at low temperatures for the suppression of the isomerization.

Figure 10 illustrates time profiles of the monomer conversion and the polymer cis content in the polymerization by $MoCl_5$-based catalysts and $Mo(CO)_6$–CCl_4–$h\nu$ catalyst. The polymerization by $MoCl_5$-based catalysts showed tendencies similar to those by the $MoOCl_4$-based counterparts. That is to say, the addition of cocatalysts augmented the polymerization rate and diminished the isomerization rate. In the $Mo(CO)_6$-catalyzed polymerization, the system became highly viscous, suggesting the formation of a high molecular

weight polymer. Here, the cis content remained around 80%, which is probably due to the low acidity of the system.

In conclusion, the factors controlling stereospecificity in the polymerization of tBA by molybdenum catalysts were investigated, and the following points have been clarified: (i) the propagation reaction proceeds stereospecifically, namely, so as to selectively form the cis structure, (ii) the geometric isomerization of the polymer is induced by acids, and (iii) the stereoregularity of the polymer is governed by the relative rates of polymerization and isomerization and by the polymerization time. Thus suppression of the polymer isomerization is essential to obtain a stereoregular polymer.

References and Notes

(1) Shirakawa, H.; Masuda, T.; Takeda, K. In *The Chemistry of Triple-Bonded Functional Groups, Supplement C2*; Patai, S., Ed.; Wiley: Chichester, U.K., 1994; Chapter 17.

(2) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.

(3) (a) Furlani, A.; Napoletano, C.; Russo, M. V. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 75. (b) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *20*, 1105. (c) Yang, W.; Tabata, M.; Yokota, K.; Shimizu, A. *Polym. J.* **1991**, *23*, 1335.

(4) Tabata, M.; Inaba, Y.; Yokota, K.; Nozaki, Y. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 465.

(5) (a) Masuda, T.; Okano, Y.; Kuwane, Y.; Higashimura, T. *Polym. J.* **1980**, *12*, 907. (b) Okano, Y.; Masuda, T.; Higashimura, T. *Polym. J.* **1982**, *14*, 477.

(6) Nakano, M.; Masuda, T.; Higashimura, T. *Macromolecules* **1994**, *27*, 1344.

(7) (a) Sowa, J. R.; Lamby, E. J.; Calamai, E. C.; Benko, P. A.; Gordinier, A. *Org. Prep. Proced. Int.* **1975**, *7*, 137. (b) Okano, Y.; Masuda, T.; Higashimura, T. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1181.

(8) (a) Yamanobe, T.; Ando, I.; Chûjô, R. *Polym. J.* **1982**, *14*, 827. (b) Leclerc, M.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2021. (c) Leclerc, M.; Prud'homme, R. E.; Soum, L.; Fontanille, M. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2031.

(9) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(10) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169.

(11) Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983; p 140.

MA951187V