NOTES

Living Polymerization of [*o*-(Trimethylsilyl)phenyl]acetylene by Molybdenum-Based Three-Component Catalysts

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Living polymerization induced by transition-metal catalysts has recently made great progress. For instance, Grubbs¹ and Schrock² have developed many living systems in ring-opening metathesis polymerization (ROMP) of cycloolefins by using well-defined metal-carbene initiators. The authors have found that molybdenum-based three-component catalysts, *i.e.*, MoOCl₄–(or MoCl₅)–*n*-Bu₄Sn–EtOH effect living polymerization of substituted acetylenes such as 1-chloro-1-octyne^{3,4} and [*o*-(trifluoromethyl)phenyl]acetylene.⁵

Silicon-containing polyacetylenes are characterized by unique properties like high gas permeability.⁶ Examples of such polymers with high molecular weight include poly[1-(trimethylsilyl)-1-propyne] and poly[[*o*-(trimethylsilyl)phenyl]acetylene] [poly(*o*-Me₃SiPA)]. The former polymer is obtained with Nb and Ta catalysts, while the latter with Mo and W catalysts.⁷ Thus it is interesting to examine whether [*o*-(trimethylsilyl)phenyl]acetylene (*o*-Me₃SiPA) will afford a living polymer or not by use of the Mo-based three-component catalysts.

In the present note, we report on the living polymerization of *o*-Me₃SiPA effected

by MoCl₅- and MoOCl₄-based catalysts and the effects of polymerization conditions on the molecular weight distribution (MWD) of polymers. The living nature of the polymerization by MoCl₅–(or MoOCl₄)–*n*-Bu₄Sn–EtOH catalysts has been proved by both small polydispersity ratios close to unity and increases of polymer molecular weight proportional to monomer consumption.

EXPERIMENTAL

The synthesis of *o*-Me₃SiPA followed the same method as described previously.⁸ The monomer was distilled twice at reduced pressure from calcium hydride before use: bp 85°C/10 mmHg, purity >99% (by gas chromatography (GC)). Transition metal chlorides (Strem Chemicals; purity >99%) and organometallic cocatalysts were commercially obtained, and used without further purification with care being taken not to be decomposed by moisture and/or air. Oxygen-containing compounds such as ethanol (EtOH) were distilled before use. Toluene as polymerization solvent was purified by a standard method.

All the procedures for polymerization were

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carried out under dry nitrogen with use of pre-baked flasks equipped with a three-way stopcock. The catalyst solution was prepared by dissolving MoCl_5 (or MoOCl_4) and $n\text{-Bu}_4\text{Sn}$ in toluene, aging at 30°C for 15 min, then adding EtOH, and finally aging at 30°C for an additional 15 min. Detailed polymerization procedures were described before.⁵ Monomer conversions were determined by measuring the initial and final monomer concentrations by GC (silicone DC 3 m, 170°C).

The MWD curves of polymers were observed by gel permeation chromatography (GPC) using a Jasco Trirotar liquid chromatograph (Shodex A803, A804, and A805 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 by MoCl_5 -Based Catalysts

Polymerization of $o\text{-Me}_3\text{SiPA}$ by MoCl_5 -based catalysts was studied using three kinds of catalysts, *i.e.*, MoCl_5 alone, $\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}$ (1:1) and $\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}\text{-EtOH}$ (1:1:0.5). The polymerizations were carried out in toluene at 30°C for 1 h, and 100% monomer conversions were observed irrespective of the number of catalyst components. As seen in Figure 1, three-component catalyst, $\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}\text{-EtOH}$ produced a polymer whose polydispersity ratio is smaller than 1.1, whereas the MWDs with the two other catalyst systems, were rather broad ($\bar{M}_w/\bar{M}_n > 1.3$). Smaller amounts of polymer having higher molecular weight were formed in the polymerizations using MoCl_5 and $\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}$, but no such fraction formed with $\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}\text{-EtOH}$. Thus, the $\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}\text{-EtOH}$ catalyst proved to yield poly($o\text{-Me}_3\text{SiPA}$) with narrow MWDs. Hence, a detailed study was carried out as shown below

Figure 1. MWD curves of poly($o\text{-Me}_3\text{SiPA}$)s obtained with MoCl_5 -based catalysts (polymerized in toluene at 30°C for 1 h; $[\text{M}]_0 = 0.50\text{ M}$; the conversions 100%).

Figure 2. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly($o\text{-Me}_3\text{SiPA}$) as a function of monomer conversion in the “monomer addition experiment” with use of $\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}\text{-EtOH}$ (1:1:0.5) (polymerized in toluene at 30°C for 1 h; $[\text{M}]_0 = [\text{M}]_{\text{added}} = 0.50\text{ M}$; $[\text{MoCl}_5] = 20\text{ mM}$).

by using this three-component catalyst.

Living nature of the polymerization was examined by so called “monomer addition experiment” (Figure 2). The $\bar{M}_n$ of polymer increases in proportion to conversion and also in the second stage where additional monomer is supplied to a polymerization system after all the monomer has been consumed. Since the polydispersity ratio of polymer remained small, this polymerization is concluded to be living.

Table I. Effect of Cocatalysts on the Polymerization of *o*-Me₃SiPA by MoCl₅-cocatalyst-EtOH (1 : 1 : 0.5)^a

Cocatalyst	Time	Conversion		Polymer ^b		
	min	%	Yield/%	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	[P*]/[Mo]
<i>n</i> -Bu ₄ Sn	60	100	88	43,000	1.07	0.010
Me ₄ Sn	60	100	96	64,000	1.11	0.068
Ph ₄ Sn	180	54	47	86,000	1.47	0.051
Et ₃ SiH	60	81	67	79,000	1.21	0.055

^a Polymerized in toluene at 30°C: [M]₀ = 0.50 M; [MoCl₅] = 20 mM.^b MeOH-insoluble part.**Table II.** Effect of Oxygen-Containing Compounds (O-compd) on the Polymerization of *o*-Me₃SiPA by MoCl₅-*n*-Bu₄Sn-O-compd (1 : 1 : 0.5)^a

O-compd	Time	Conversion		Polymer		
	min	%	Yield/%	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	[P*]/[Mo]
None	60	100	95	99,000	1.31	0.048
EtOH	60	100	88	43,000	1.07	0.10
CH ₃ COOH	60	100	94	66,000	1.11	0.066
CH ₃ COO- <i>n</i> -Bu	60	100	95	73,000	1.14	0.060
Acetone	60	100	95	69,000	1.24	0.063
H ₂ O	120	98	95	97,000	1.12	0.045

^a Polymerized in toluene at 30°C: [M]₀ = 0.50 M; [MoCl₅] = 20 mM.

Table I shows the effect of some organo-metallic cocatalysts on the polymerization of *o*-Me₃SiPA by MoCl₅-cocatalyst-EtOH (1 : 1 : 0.5). The MWDs of the polymers were quite narrow with use of *n*-Bu₄Sn and Me₄Sn as cocatalysts. In contrast, Ph₄Sn, and Et₃SiH as cocatalysts gave polymers with rather broad MWDs ($\bar{M}_w/\bar{M}_n$ ca. 1.2—1.5). Further, the latter two cocatalysts depressed the monomer conversion. These clearly show that the activity of the MoCl₅-cocatalyst-EtOH system strongly depends on the nature of cocatalyst. At present it is virtually accepted that the propagating species of the polymerization are metal carbenes. Hence one can assume from the propagating end-to-catalyst ratios ([P*]/[Mo]) in Table I that *n*-Bu₄Sn as cocatalyst provides the most stable metal carbene.

Table II details the results of the effect of

oxygen-containing compounds on the polymerization of *o*-Me₃SiPA. Oxygen-containing compounds other than acetone as third components of catalyst gave fairly small values of $\bar{M}_w/\bar{M}_n$ (~1.1). This finding means that the oxygen-containing compounds are useful for the formation of stable metal carbenes. It is worth noting that acetic acid, *n*-butyl acetate and H₂O show similar effectiveness to one another on the basis of their $\bar{M}_w/\bar{M}_n$ ratios (~1.1). This suggests that the presence of a labile proton in the oxygen-containing compound is not necessarily required for living polymerization of *o*-Me₃SiPA.

Polymerization by MoOCl₄-Based Catalysts

Previous studies have shown that the effects of MoOCl₄-based catalysts on the polymerization of substituted acetylenes resemble those with the MoCl₅-based counterpart.^{3,5} How-

Figure 3. MWD curves of poly(*o*-Me₃SiPA)s obtained with MoOCl₄-based catalysts (polymerized in toluene at 30°C for 1 h; [M]₀ = 0.50 M; the conversions 100%).

ever, better results with respect to living polymerization have been obtained with MoOCl₄ than with MoCl₅. It has also been found through molecular orbital calculations that the presence of metal-oxygen bond provides higher stabilities of metal carbene and metalla-cyclobutane and effects the metathesis reaction more smoothly.⁹ Thus the following studies were carried out to further examine the above phenomena in the polymerization of *o*-Me₃SiPA using MoOCl₄-based catalysts. For the sake of comparison, the polymerization reactions were carried out under the same conditions as for MoCl₅-based catalysts.

As seen in Figure 3, the $\bar{M}_w/\bar{M}_n$ of polymer was below 1.10 with the MoOCl₄-*n*-Bu₄Sn-EtOH catalyst, but the ratios with MoOCl₄-*n*-Bu₄Sn and MoOCl₄ alone as catalysts were larger, *i.e.*, 1.11 and 1.21, respectively. Formation of a higher molecular weight fraction was not observed in these polymerizations using MoOCl₄-based catalysts.

Livingness of the propagating species in the polymerization by MoOCl₄-*n*-Bu₄Sn-EtOH was confirmed by a narrow MWD and an increase of polymer molecular weight proportional to monomer consumption (Figure 4). When compared with the polymerization by MoCl₅-*n*-Bu₄Sn-EtOH (see Figure 1), both

Figure 4. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(*o*-Me₃SiPA) as a function of monomer conversion in the "monomer addition experiment" with use of MoOCl₄-*n*-Bu₄Sn-EtOH (1:1:0.5) (polymerized in toluene at 30°C for 1 h; [M]₀ = [M]_{added} = 0.50 M; [MoOCl₄] = 20 mM).

give the same polydispersity ratio of 1.07. However, more perfect living polymerization can be achieved by using MoOCl₄-*n*-Bu₄Sn-EtOH than MoCl₅-*n*-Bu₄Sn-EtOH from the viewpoint of the ratio of the propagating species to the Mo catalyst ([P*]/[Mo]), *i.e.*, initiator efficiency. That is, the [P*]/[Mo] ratio was 0.13 for MoOCl₄-*n*-Bu₄Sn-EtOH, which is larger than 0.08 for MoCl₅-*n*-Bu₄Sn-EtOH (see Figures 2 and 3).

CONCLUSIONS

The MoCl₅-(or MoOCl₄)-*n*-Bu₄Sn-EtOH catalyst systems effected living polymerization of *o*-Me₃SiPA to give polymers with narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.1$). In these polymerizations, the $\bar{M}_n$ of polymer increased in direct proportion to monomer conversion and even after additional monomer was supplied to a completely polymerized system. As living polymerization catalyst, MoOCl₄-*n*-Bu₄Sn-EtOH surpassed MoCl₅-*n*-Bu₄Sn-EtOH on the basis of their initiator efficiencies ([P*]/[Mo] = 0.13 *vs.* 0.08).

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