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Synthesis of poly[1-(trimethylsilyl)-1-propyne] with a narrow molecular weight distribution by using $NbCl_5$ catalyst in cyclohexane

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SUMMARY

The polymerization of 1-(trimethylsilyl)-1-propyne [$CH_3C\equiv CSi(CH_3)_3$] catalyzed by $NbCl_5$ in cyclohexane solution produced a polymer having a narrow molecular weight distribution (MWD). In this polymerization, the number-average molecular weight ($\bar{M}_n$) of the polymer increased in direct proportion to conversion, while the MWD of the polymer remained narrow ($\bar{M}_w/\bar{M}_n \sim 1.2$) irrespective of the conversion. Poly[1-(trimethylsilyl)-1-propyne]s having narrow MWD and $\bar{M}_n$ in the range 1×10^4 - 20×10^4 could be obtained by changing the ratio of monomer to catalyst. Thus, the present polymerization involves a long-lived propagating species, and provides a useful method for synthesizing poly[1-(trimethylsilyl)-1-propyne] with a narrow MWD.

INTRODUCTION

Thus far there have been only a few studies on the living polymerization initiated by transition metal catalysts; i.e., polymerization of cycloolefin by Ti, Ta and W catalysts,[1] polymerization of propene by V catalysts,[2] and polymerization of 1,3-butadiene by Ni catalysts.[3] Quite recently, we have found that the living polymerization of 1-chloro-1-alkynes takes place in the presence of $MoCl_5$(or $MoOCl_4$)-nBu_4Sn-EtOH catalysts.[4]

1-(Trimethylsilyl)-1-propyne, which is a Si-containing disubstituted acetylene, polymerizes with $TaCl_5$ and $NbCl_5$ to produce a high-molecular-weight polymer.[5] The polymer formed exhibits interesting properties such as extremely high oxygen permeability.[6] Recently, it was claimed that the polymerization of 1-(trimethylsilyl)-1-propyne by $TaCl_5$ was living on the basis of molecular weight increase with conversion,[7] but the MWD of the polymer was broad [dispersity ratio ($\bar{M}_w/\bar{M}_n$ > 2)]. So far, we have observed many cases where the $\bar{M}_n$ of the polymer increases with conversion in the polymerization of substituted acetylenes by groups 5 and 6 transition-metal catalysts: $MeC\equiv CSiMe_2CH_2SiMe_3/TaCl_5$,8) $RC\equiv CPh/TaCl_5$,9) $HC\equiv CPh\text{-}o\text{-}CF_3/MoCl_5\text{-}Ph_4Sn$.10) In general, however, the MWD of the polymer produced is broad. Therefore, these polymerizations may involve long-lived propagating species, but they are not true living polymerizations.

In the course of our detailed study on the polymerization of 1-(trimethylsilyl)-1-propyne, we found that the $NbCl_5$ catalyst produced a polymer with narrow MWD ($\bar{M}_w/\bar{M}_n \sim 1.2$) when a particular solvent of cyclohexane was employed. This observation prompted us to study the polymerization system in more detail. The present paper reveals the living nature of the polymerization of 1-(trimethylsilyl)-1-propyne by $NbCl_5$ in cyclohexane on the basis of both the narrow MWD of the polymer and the increase in the number-average molecular weight of the polymer proportional to conversion.

EXPERIMENTAL

1-(Trimethylsilyl)-1-propyne was offered by Shin-etsu Chemical Industries Ltd, Japan, and was distilled twice from calcium hydride; purity >99.8% [by gas chromatography (GC)]. Catalysts [halides of Nb(V) and Ta(V); from Alfa Products] were used without further purification.

Polymerizations were carried out under dry nitrogen according to the procedure described before.[5] Unless otherwise specified, a polymerization temperature of 75°C was employed, at which the polymer yield was high and the long-lived propagating species was observed. The catalyst solution was aged for 15 min before use. Polymers formed were precipitated into a large amount of methanol, filtered, and dried to constant weights under vacuum. The monomer conversion was determined by GC. The polymer yield was determined by gravimetry. In some cases, a small amount of methanol-soluble oligomers were produced; the molecular weight measurements were carried out only with the methanol-insoluble polymer. The MWD curves of polymers were observed by gel permeation chromatography (GPC); Jasco Trirotar Chromatograph, eluent $CHCl_3$, Shodex A804, A806, A807 polystyrene gel columns. 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

At first it was studied what catalyst and solvent would achieve the living polymerization of 1-(trimethylsilyl)-1-propyne. Then the behavior of the polymerization by $NbCl_5$ in cyclohexane which proved to be a living system was examined in detail.

Table I
Effect of Catalysts on the Polymerization of 1-(Trimethylsilyl)-1-propyne in Cyclohexane[a]

		Polymer[b]		
Catalyst	Conversion (%)	Yield (%)	$\bar{M}_n$[c] / 10^3	$\bar{M}_w$[c] / $\bar{M}_n$
$NbCl_5$	100	100	123	1.17
$TaCl_5$	100	100	567	3.36
$NbBr_5$	100	61	- d	-
$TaBr_5$	93	81	- d	-

a) Polymerized at 75°C for 24 h; $[M]_o$ = 1.0 M, [Cat] = 20 mM.
b) Methanol-insoluble products.
c) Determined by GPC.
d) Virtually insoluble in toluene.

Table II
Effect of Solvents on the Polymerization of
1-(Trimethylsilyl)-1-propyne by $NbCl_5$[a]

		Polymer[b]		
Solvent	Conversion (%)	Yield (%)	$\frac{\bar{M}_n{}^c}{10^3}$	$\frac{\bar{M}_w{}^c}{\bar{M}_n}$
cyclohexane	100	100	123	1.17
cyclooctane	100	70	91	1.21
decalin	100	76	148	1.27
toluene	100	100	173	1.36
n-heptane	100	76	158	1.46
CCl_4	100	72	90	1.56

a) Polymerized at 75°C for 24 h; $[M]_o = 1.0$ M, [Cat] = 20 mM.
b) Methanol-insoluble products.
c) Determined by GPC.

Effect of Catalysts and Solvents

Table I shows results on the polymerization of 1-(trimethylsilyl)-1-propyne by Nb and Ta catalysts in cyclohexane. $NbCl_5$ and $TaCl_5$ afforded virtually quantitatively poly[1-(trimethylsilyl)-1-propyne]s which were completely soluble in many organic solvents such as toluene and chloroform. $NbCl_5$ provided a polymer having a $\bar{M}_n$ of about 1×10^5 and a narrow MWD ($\bar{M}_w/\bar{M}_n \sim 1.2$). This finding suggests that the polymerization is a living system. Though the polymer obtained with $TaCl_5$ possessed a higher molecular weight, its MWD was broad ($\bar{M}_w/\bar{M}_n > 2$). $NbBr_5$ and $TaBr_5$ gave only polymers partly or totally insoluble in any solvents.

The effect of solvents on the polymerization by $NbCl_5$ was studied (Table II). Poly[1-(trimethylsilyl)-1-propyne]s were obtained in high yields in all the solvents in Table II, although in some cases methanol-soluble oligomers were produced to some extent. The $\bar{M}_n$ values of the polymers were in the range of ca. 10×10^4 - 17×10^4. The MWD of the polymer formed in cyclohexane was the narrowest ($\bar{M}_w/\bar{M}_n < 1.2$). The MWD's of the polymer obtained in analogous cycloalkanes were also relatively narrow ($\bar{M}_w/\bar{M}_n$ 1.2-1.3). In contrast, the MWD's of the polymers obtained in n-heptane, toluene and carbon tetrachloride were broader ($\bar{M}_w/\bar{M}_n > 1.3$), although their polarities are similar to that of cyclohexane.

The results shown above lead to a conclusion that $NbCl_5$ is suitable as catalyst and cyclohexane as solvent to obtain poly[1-(trimethylsilyl)-1-propyne] having a narrow MWD.

On the Living Nature of Polymerization

Figure 1 shows the $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of polymer as functions of conversion in the polymerization of 1-(trimethylsilyl)-1-propyne by $NbCl_5$ in cyclohexane. The $\bar{M}_n$ of the polymer increased in direct proportion to conversion. The ratio of active species to catalyst ([P*]/[Cat]), which was calculated on the basis of monomer conversion, was 0.048. The line for $\bar{M}_n$ in Figure 1a stands for the theoretical variation of $\bar{M}_n$ with conversion in the case where [P*]/[Cat] is 0.048. The MWD of the polymer remained

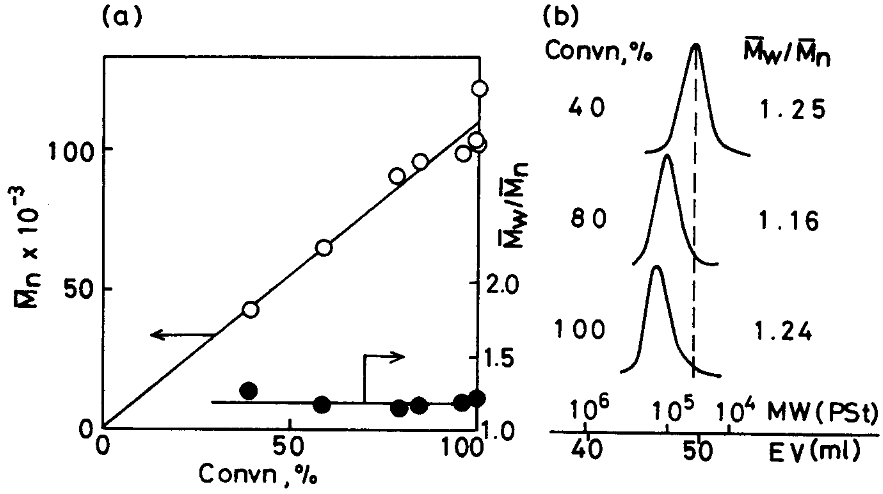

Figure 1. $\bar{M}_n$ and MWD of poly[1-(trimethylsilyl)-1-propyne] as functions of monomer conversion (NbCl$_5$, in cyclohexane, 75°C; $[M]_0$ = 1.0 M, [Cat] = 20 mM). The line for $\bar{M}_n$ is based on [P*]/[Cat] = 0.048 (see the text).

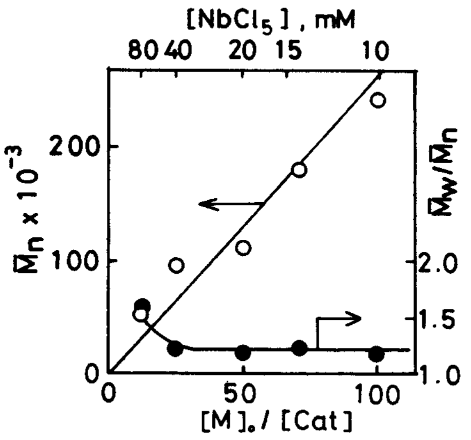

Figure 2. Changes in the $\bar{M}_n$ and MWD of poly[1-(trimethylsilyl)-1-propyne] with catalyst concentration (NbCl$_5$, in cyclohexane, 75°C, $[M]_0$ = 1.0 M). The line for $\bar{M}_n$ is based on [P*]/[Cat] = 0.048 (see the text).

narrow ($\bar{M}_w/\bar{M}_n \sim 1.2$) irrespective of conversion. The GPC curve in Figure 1b showed a sharp single peak, which shifted toward the higher molecular weight side without tailing as the conversion increased. These results demonstrate that living polymerization of 1-(trimethylsilyl)-1-propyne takes place.

Control of $\bar{M}_n$ of the produced polymer was tried by changing catalyst concentration while keeping the monomer concentration constant ($[M]_0$ = 1.0 M) (Figure 2). The $\bar{M}_n$ of the polymer at 100% conversion was directly proportional to the monomer-to-catalyst ratio ($[M]_0$/[Cat]). The line for $\bar{M}_n$ in Figure 2 designates the theoretical one in the case of [P*]/[Cat] = 0.048. The MWD remained relatively narrow ($\bar{M}_w/\bar{M}_n \sim 1.2$) over a range of $[M]_0$/[Cat] = 25-100. This result also supports the idea that this polymerization is a living system. It was possible to prepare poly[1-(trimethylsilyl)-1-propyne] which has

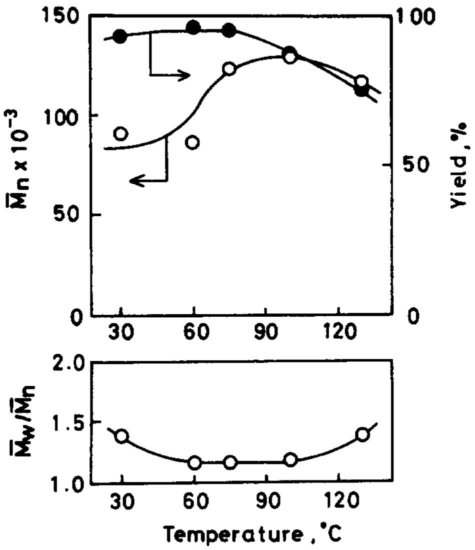

Figure 3. Effects of temperature on the polymerization of 1-(trimethylsilyl)-1-propyne [$NbCl_5$, in cyclohexane (30-75°C) or decalin (100-130 °C), 5 h, $[M]_0 = 1.0$ M, [Cat] = 20 mM].

a narrow MWD and a $\bar{M}_n$ in the range of 1×10^4 - 20×10^4 by selecting not only the concentration of monomer but also that of catalyst.

In the perfect living polymerization, the $\bar{M}_n$ of the polymer continues to increase when the second feed of monomer is supplied to the system after the initial feed has been consumed. The so-called "monomer addition" experiment was attemped to examine the living nature of the present polymerization. The MWD of the produced polymer, however, was bimodal (the low-molecular-weight peak: $\bar{M}_n = 8 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.26$; the high-molecular-weight peak: $\bar{M}_n = 54 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.34$). Since the low-molecular-weight peak did not shift after the monomer re-addition, it is inferred that this peak stems from the propagating species which was deactivated when the second monomer feed was supplied. The high-molecular-weight peak appeared after the monomer re-addition; this indicates that a part of the propagating species survived, with which polymerization continued. The proportion of the survived propagating species was ca. 20% against the concentration of propagating species before the second monomer addition according to the peak areas in the GPC curve and their molecular weights. The deactivation of a part of the propagating species should be due either to the nature of this polymerization system or to impurities included in the second monomer feed.

Figure 3 shows the effect of temperature on the polymerization. The polymer yield was high, and the MWD of the polymer was narrow at 75°C. The polymer yield decreased and the MWD of the polymer was broad at 130°C. This is attributable to the deactivation of some of the propagating species at such a high temperature. The MWD of the polymer obtained at 30°C was also broad, the reason of which is not clear at present. Consequently, a temperature around 75°C is the most suitable to obtain a polymer having a narrow MWD.

CONCLUSION

In summary, the present study disclosed that the polymerization of 1-(trimethylsilyl)-1-propyne by $NbCl_5$ as catalyst in cyclohexane at 75°C forms a long-lived propagating species to give a polymer having a narrow MWD ($\bar{M}_w/\bar{M}_n \sim 1.2$). The result obtained indicates that it is possible to improve the living nature of the propagating species in the polymerization of the substituted acetylenes by selecting polymerization conditions such as solvent. The polymerization in the present study provides a useful method for preparing poly[1-(trimethylsilyl)-1-propyne] which has a narrow MWD.

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