Macromolecules **1985**, *18*, 2109–2113

References and Notes

(1) Halpern, B. D.; Solomon, O.; Chowhan, D. G. Contract No. N01-HV-6-1124, 1976.

(2) Qiu, K. Y.; Yang, F. L.; Huang, Z. X.; Feng, X. J. Feng, X. D. *Polym. Commun.* **1982**, *2*, 81.

(3) Sun, Y. H. Ph.D. thesis submitted to Peking University, Beijing, China, 1984.

(4) Sun, Y. H.; Qiu, K. Y.; Feng, X. D. *Polym. Commun.* **1983**, *2*, 81.

(5) Adibi, K., et al. *Polymer* **1979**, *20*, 483.

(6) Narita, H.; Okimoto, T.; Mechida, S. *Makromol. Chem.* **1974**, *175*, 111.

(7) Ohtsuka, Y.; Kawagushi, H.; Tokunaga, K. *Kobunshi Ronbunshu* **1975**, *32*(8), 472.

Effect of Organometallic Cocatalysts on the Polymerization of 1-Phenyl-1-propyne by $TaCl_5$ and $NbCl_5$[1]

Toshio Masuda,* Akihiro Niki, Eiji Isobe, and Toshinobu Higashimura*

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

Received March 25, 1985

ABSTRACT: In the polymerization of 1-phenyl-1-propyne by $TaCl_5$, the polymer formed underwent degradation after all the monomer had been consumed. In contrast, no polymer degradation occurred when suitable organometallics (e.g., tetra-*n*-butyltin, triethylsilane, and triphenylbismuth) were added as cocatalysts at 1:1 ratio to $TaCl_5$. Consequently, polymers with weight-average molecular weights ($\bar{M}_w$) exceeding 1×10^6 could be obtained. Further, use of cocatalysts considerably accelerated the polymerization. Thus a facile method for synthesizing high-molecular-weight poly(1-phenyl-1-propyne) has been established. Polymer degradation was observed also in the polymerization of 1-phenyl-1-propyne by $NbCl_5$, and it was restrained by use of cocatalysts resulting in the formation of polymers with $\bar{M}_w$ around 3×10^5.

1-Phenyl-1-propyne polymerizes in the presence of group 6 transition-metal catalysts, that is, $Mo(CO)_3$·toluene[3] and 1:1 WCl_6–Ph_4Sn[4,5] (see eq 1). However, the molecular weights of the products are no more than several thousand; thus they are so-called oligomers.

$$CH_3C{\equiv}CC_6H_5 \xrightarrow{\text{catalyst}} \left[\underset{CH_3}{\underset{|}{C}} = \underset{C_6H_5}{\underset{|}{C}} \right]_n \qquad (1)$$

Niobium (Nb) and tantalum (Ta) are group 5 transition metals and are located immediately to the left of molybdenum and tungsten, respectively, in the periodic table. It has been reported that organo–Nb(III) and –Ta(III) binuclear complexes, $M_2Cl_6(SC_4H_8)_3$ (M = Nb, Ta), polymerize 1-phenyl-1-propyne to high polymers.[6] These complexes are, however, rather difficult to prepare and unstable to air.

The pentachlorides of Nb and Ta induce 1-phenyl-1-propyne to polymerize, and the maximum weight-average molecular weight ($\bar{M}_w$) of the polymer reaches ca. 6×10^5.[2,7] However, this polymerization system had the problem that polymer degradation occurs after all the monomer has reacted, resulting in the complete conversion to oligomers.[2] Thus there was no easy method for preparing high-molecular-weight poly(1-phenyl-1-propyne).

This paper reports on cocatalyst effects of the polymerization of 1-phenyl-1-propyne by $TaCl_5$ and $NbCl_5$. Various organometallics were examined as cocatalysts; they are expected to function as weak reducing agents and as ligands on the active species. Consequently, it was found that they not only accelerate polymerization but also effectively inhibit polymer degradation. Thus a facile method has been established for synthesizing poly(1-phenyl-1-propyne) with $\bar{M}_w$ exceeding one million.

Experimental Section

Materials. 1-Phenyl-1-propyne was purchased from Farchan Labs. and distilled twice at reduced pressure from calcium hydride before use. $NbCl_5$ and $TaCl_5$ were purchased from Alfa, Morton Thiokol, Inc., and used without further purification. Organometallics as cocatalysts were commercially obtained and usually employed without further purification. Polymerization solvents were purified by standard methods, care being taken to remove moisture as completely as possible.

Polymerization. Polymerizations were carried out under dry nitrogen. A typical procedure is as follows (cf. Table I, third row): A monomer solution was prepared by adding 1-phenyl-1-propyne (1.39 g, 1.50 mL, 12.0 mmol) and bromobenzene (0.40 mL, as internal standard for gas chromatography (GC)) to toluene (4.10 mL). A catalyst solution was prepared by mixing $TaCl_5$ (71.6 mg, 0.20 mmol) and tetra-*n*-butyltin (*n*-Bu_4Sn; 69.4 mg, 0.20 mmol) in toluene (5.0 mL) and aged by keeping at 80 °C for 15 min. Then 5 mL of the monomer solution (the residual monomer solution was used for GC) was added to the catalyst solution at 80 °C. After 24 h, the reaction was terminated by adding a mixture of toluene (5 mL) and methanol (0.5 mL). Conversion was determined by measuring the initial and final monomer concentrations through GC (silicone DC 1 m, 140 °C); 100%. The polymerization solution was diluted with toluene (100 mL) and poured into acetone (1 L); methanol, which is often used as a polymer precipitant, was not used because cyclotrimers of 1-phenyl-1-propyne (byproducts) also precipitated in methanol. The polymer was filtered off, washed with acetone, and dried to a constant weight under vacuum. The polymer yield was determined by gravimetry; 76%.

Molecular Weight Measurement. Number-average molecular weights ($\bar{M}_n$) and $\bar{M}_w$ were evaluated by gel permeation chromatography (GPC) using a Jasco Triroter high-performance liquid chromatograph (Shodex A802, A804, A806 polystyrene gel columns, eluent $CHCl_3$, polystyrene calibration). It is known[2] that the $\bar{M}_w$ of poly(1-phenyl-1-propyne) tentatively obtained by GPC on the basis of polystyrene calibration is ca. 1.5 times as large as the "true" $\bar{M}_w$ determined by the light-scattering method.

Results

Polymerization by $TaCl_5$. Figure 1 shows time changes of conversion and polymer $\bar{M}_w$ in the polymerization of 1-phenyl-1-propyne by $TaCl_5$ alone.[8] Under the conditions shown in Figure 1, conversion reached 100% at about 6 h. The $\bar{M}_w$ of polymer increased with increasing conversion to become ca. 6×10^5 at 100% conversion.[9] However, when the reaction system was allowed to stand for longer periods, $\bar{M}_w$ dramatically decreased to no more than several thousand after 24 h.

Changes in molecular weight distribution (MWD) with time are shown in Figure 2. The MWD peak was located at several hundred thousand at 6 h, that is, at the time

0024-9297/85/2218-2109$01.50/0

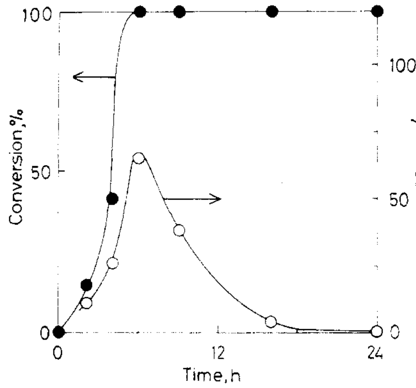


Figure 1. Time dependences of conversion and polymer molecular weight in the polymerization of 1-phenyl-1-propyne by $TaCl_5$ (in toluene, 80 °C, $[M]_0$ = 1.0 M, [Cat.] = 20 mM).

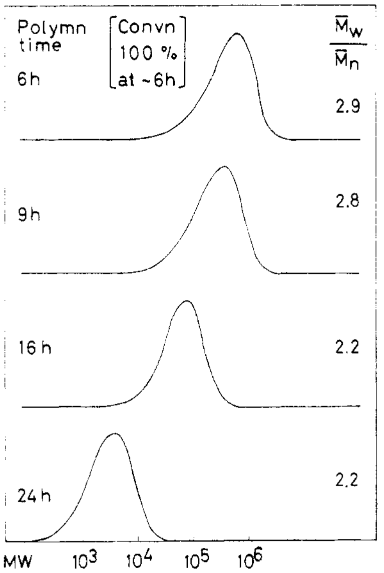


Figure 2. Molecular weight distribution of poly(1-phenyl-1-propyne) during polymerization by $TaCl_5$ (in toluene, 80 °C, $[M]_0$ = 1.0 M, [Cat.] = 20 mM).

when all the monomer had been consumed. Then polymer degradation started, and $\bar{M}_w$ shifted to several thousand after 24 h. The polydispersity ratio, $\bar{M}_w/\bar{M}_n$, remained within 2–3 over the course of this polymer degradation, indicating that the degradation is occurring randomly.

No polymer degradation took place when a toluene solution of isolated poly(1-phenyl-1-propyne) was left in the absence of $TaCl_5$. And, if $TaCl_5$ was added to this polymer solution, polymer degradation was observed. This leads to the conclusion that the present polymer degradation is induced by Ta-based species.

Polymerization by $TaCl_5$–n-Bu_4Sn. It is known that n-Bu_4Sn serves as an effective cocatalyst in the polymerizations of 2-alkynes[10] and 1-chloro-2-phenylacetylene[11] by $MoCl_5$; that is, high-molecular-weight polymers can be obtained only in the presence of suitable organometallic cocatalysts such as n-Bu_4Sn. This fact prompted us to study the effect of n-Bu_4Sn as a cocatalyst in the polymerization of 1-phenyl-1-propyne by $TaCl_5$.

Figure 3 shows time courses of conversion and $\bar{M}_w$ for the polymerization by a 1:1 mixture of $TaCl_5$ and n-Bu_4Sn. The polymerization conditions are the same as in Figure 1. Polymerization was dramatically accelerated by addition of the cocatalyst; that is, conversion reached 100% in 5 min, whereas it took 6 h in the absence of the cocatalyst.

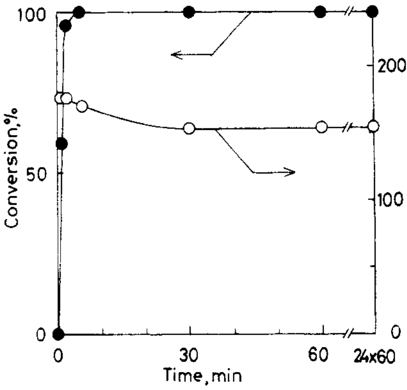


Figure 3. Time dependences of conversion and polymer molecular weight in the polymerization of 1-phenyl-1-propyne by $TaCl_5$–n-Bu_4Sn (in toluene, 80 °C, $[M]_0$ = 1.0 M, [Cat.] = [Cocat.] = 20 mM).

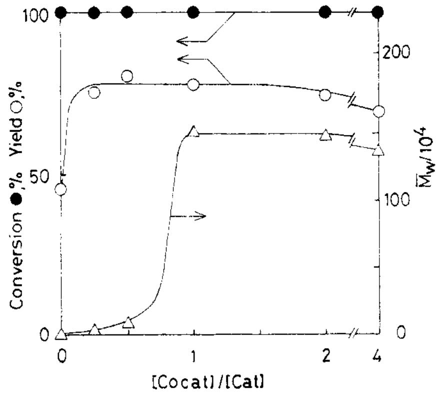


Figure 4. Effect of cocatalyst-to-catalyst ratio on the polymerization of 1-phenyl-1-propyne by $TaCl_5$–n-Bu_4Sn (in toluene, 80 °C, 24 h, $[M]_0$ = 1.0 M, [Cat.] = 20 mM).

As is clear from Figure 3, the $\bar{M}_w$ of the polymer formed lay in the range 1.5×10^6 to 1.7×10^6 irrespective of polymerization time and did not appreciably decrease after 100% conversion. This demonstrates that use of an appropriate cocatalyst restrains the polymer degradation after polymerization. Furthermore it should be noted that these $\bar{M}_w$ values of 1.5×10^6 to 1.7×10^6 are higher than the maximum $\bar{M}_w$ of ca. 6×10^5 attained with $TaCl_5$ alone just when conversion has reached 100%.

It was studied how much n-Bu_4Sn as cocatalyst is adequate to suppress the polymer degradation (Figure 4). Conversion was quantitative irrespective of the absence or presence of n-Bu_4Sn under the conditions in Figure 4. The yield of acetone-insoluble polymer was ca. 50% in the absence of n-Bu_4Sn, while ca. 75% in its presence. The acetone-soluble product consisted mainly of cyclotrimers according to GPC and ^1H NMR spectra. When $[n\text{-}Bu_4Sn]/[TaCl_5] \geq 1$, polymer degradation was restrained, and eventually poly(1-phenyl-1-propynes) with $\bar{M}_w \simeq 1.5 \times 10^6$ were obtained. On the other hand, in the case where $[n\text{-}Bu_4Sn]/[TaCl_5] < 1$, the polymers formed degraded, and their $\bar{M}_w$ values after 24 h were only 2×10^3 to 1×10^5. Thus the conclusion can be reached that there should be more cocatalyst than catalyst to effectively inhibit the polymer degradation.

The monomer-to-catalyst ratio was changed from 12.5 to 200 by choosing monomer and catalyst concentrations in the polymerization by 1:1 $TaCl_5$–n-Bu_4Sn (Table I, nos. 1–5). Consequently, the conversions were all 100% and the polymer yields were ca. 70–90%, whereas $\bar{M}_w$ increased from 0.4×10^6 to 3.4×10^6, that is, by about 10 times. $\bar{M}_w = 3.4 \times 10^6$ corresponds to a degree of polymerization of 29000, which is by far larger than the monomer-to-catalyst ratio of 200. This indicates that the concentration of active species is much lower than that of catalyst.

Table I
Effects of Monomer and Catalyst Concentrations and Temperature on the Polymerization of 1-Phenyl-1-propyne by 1:1 $TaCl_5$–*n*-Bu_4Sn[a]

						polymer		
no.	$[M]_0$, M	[Cat.], mM	$[M]_0$/[Cat.]	temp, °C	convn, %	yield, %	$\bar{M}_w/10^3$ [b]	$\bar{M}_n/10^3$ [b]
1	0.25	20	12.5	80	100	68	400	190
2	0.5	20	25	80	100	93	1200	480
3	1	20	50	80	100	76	1500	600
4	1	10	100	80	100	82	2200	880
5	1	5	200	80	100	90	3400	1600
6	1	20	50	30	100	73	1600	720
7	1	20	50	60	100	87	1700	650
8	1	20	50	100	100	89	120	47

[a] Polymerized in toluene for 24 h. [b] Determined by GPC.

Table II
Solvent Effects on the Polymerization of 1-Phenyl-1-propyne by $TaCl_5$–*n*-Bu_4Sn[a]

		polymer		
solvent	convn, %	yield, %	$\bar{M}_w/10^3$ [b]	$\bar{M}_n/10^3$ [b]
toluene	100	76	1500	600
cyclohexane	100	77	1100	360
$(CH_2Cl)_2$	100	80	770	380
CCl_4	51	7	9.3	2.8
anisole	0	0		
$PhCO_2CH_3$	0	0		
$PhCOCH_3$	0	0		

[a] Polymerized at 80 °C for 24 h; $[M]_0$ = 1.0 M, [Cat.] = [Cocat.] = 20 mM. [b] Determined by GPC.

Table III
Effects of Organotin Cocatalysts on the Polymerization of 1-Phenyl-1-propyne by $TaCl_5$[a]

		polymer		
Cocat.	convn, %	yield, %	$\bar{M}_w/10^3$ [b]	$\bar{M}_n/10^3$ [b]
none	100	47	2.6	1.2
n-Bu_4Sn	100	76	1500	600
Me_4Sn	100	82	1200	450
Ph_4Sn	100	80	1300	500
n-Bu_3SnH	100	84	1300	370
n-Bu_3SnCl	100	82	830	310
Ph_3SnCl	100	91	780	290

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 1.0 M, [Cat.] = [Cocat.] = 20 mM. [b] Determined by GPC.

Table IV
Effects of Organosilicon Cocatalysts on the Polymerization of 1-Phenyl-1-propyne by $TaCl_5$[a]

			polymer		
Cocat.	[Cocat.]/[Cat.]	convn, %	yield, %	$\bar{M}_w/10^3$ [b]	$\bar{M}_n/10^3$ [b]
none	0	100	47	2.6	1.2
Et_4Si	1.0	100	66	4.9	2.8
Et_4Si	2.0	100	68	4.9	2.7
Et_3SiH	1.0	100	86	200	84
Et_3SiH	2.0	100	75	1300	410
Ph_3SiH	1.0	100	95	520	190
Ph_3SiH	2.0	100	95	1600	750
$\lfloor SiH(CH_3)O \rfloor_n$	1.0	100	83	140	62
$\lfloor SiH(CH_3)O \rfloor_n$	2.0	100	93	980	280

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 1.0 M, [Cat.] = 20 mM. [b] Determined by GPC.

Table V
Effects of Ph_3X (X = Group 5B Elements) as Cocatalysts on the Polymerization of 1-Phenyl-1-propyne by $TaCl_5$[a]

		polymer		
Cocat.	convn, %	yield, %	$\bar{M}_w/10^3$ [b]	$\bar{M}_n/10^3$ [b]
none	100	47	2.6	1.2
Ph_3P	16	0		
Ph_3As	19	0		
Ph_3Sb	100	90	1600	850
Ph_3Bi	100	79	1800	670

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 1.0 M, [Cat.] = [Cocat.] = 20 mM. [b] Determined by GPC.

No large difference in $\bar{M}_w$ was observed among polymerization temperatures from 30 to 80 °C, while $\bar{M}_w$ decreased considerably at 100 °C (see Table I, nos. 1, 6–8). The $\bar{M}_w/\bar{M}_n$ ratios for the polymerizations in Table I are in the range 2.0–2.6, approximately corresponding to the most probable distribution.

Table II lists results for the polymerization by 1:1 $TaCl_5$–*n*-Bu_4Sn in various solvents. $\bar{M}_w$ exceeded one million in hydrocarbon solvents such as toluene and cyclohexane. Halogenated hydrocarbons did not necessarily provide high-molecular-weight polymers. No polymer was obtained at all in oxygen-containing solvents such as anisole, methyl benzoate, and acetophenone.

Effects of Various Cocatalysts. The effect of various organotin compounds as cocatalysts was examined, whose results are given in Table III. The $\bar{M}_w$ of the polymer obtained without any cocatalyst after 24-h polymerization was only ca. 3000. In the cases of *n*-Bu_4Sn, Me_4Sn, and Ph_4Sn as cocatalysts, polymers with $\bar{M}_w = 1.2 \times 10^6$ to 1.5×10^6 were obtained in ca. 80% yields. *n*-Bu_3SnH, which has a Sn–H bond, was also an active cocatalyst. Chlorine-containing organotins such as *n*-Bu_3SnCl and Ph_3SnCl afforded polymers having lower $\bar{M}_w$.

Results for organosilicon compounds as cocatalysts are shown in Table IV. Et_4Si hardly exerted a cocatalytic action. This seems due to the fact that the alkyl–Si bond is stronger than the corresponding alkyl–Sn bond. On the other hand, various organosilicons having a Si–H bond (hydrosilanes) work effectively as cocatalysts. This seems compatible with the fact that hydrosilanes serve as reagents for transition-metal-catalyzed hydrosilylation.[12] A twofold excess for hydrosilanes to the catalyst was necessary to achieve high molecular weights. Thus the ability of hydrosilanes to repress polymer degradation is somewhat weaker than that of organotins.

Triphenyl-substituted compounds of group 5 main-group elements were examined with respect to their cocatalytic activity (Table V). When Ph_3P and Ph_3As were used, polymerization hardly occurred. This is probably because they form complexes with $TaCl_5$ owing to their strong basicity to deactivate it. In contrast, Ph_3Sb and Ph_3Bi provided in 80–90% yields polymers having $\bar{M}_w = 1.6 \times 10^6$ to 1.8×10^6; thus they are effective cocatalysts.

In the olefin polymerization by Ziegler catalysts, organometallics containing group 1–3 main-group metals are usually employed as cocatalysts. Therefore, the effect of organolithiums, -borons, and -aluminums was studied (Table VI). The two lithium compounds examined were effective as cocatalysts. In the case of organoborons and -aluminums, the $\bar{M}_w$ of the polymer varied considerably,

Table VI
Effects of Li, B, and Al Compounds as Cocatalysts on the Polymerization of 1-Phenyl-1-propyne by $TaCl_5$[a]

Cocat.	convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
none	100	47	2.6	1.2
n-BuLi	100	81	1500	540
t-BuLi	100	78	1100	390
9BBN[c]	100	82	600	290
Ph_3B	100	91	130	62
Et_3Al	78	29	120	49
i-Bu_2AlH	27	9	100	46
vitride[d]	100	78	1700	630

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 1.0 M, [Cat.] = [Cocat.] = 20 mM. [b] Determined by GPC. [c] 9BBN = 9-borabicyclo[3.3.1]nonane. [d] Vitride: sodium bis(2-methoxyethoxy)aluminum hydride.

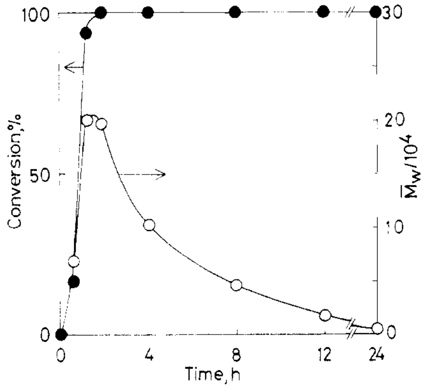


Figure 5. Time dependences of conversion and polymer molecular weight in the polymerization of 1-phenyl-1-propyne by $NbCl_5$ (in toluene, 80 °C, $[M]_0$ = 1.0 M, [Cat.] = 20 mM).

depending on individual compounds. Common organoaluminums like Et_3Al and *i*-Bu_2AlH were not very useful. When $TaCl_5$ was aged with them in the catalyst solutions, it tended to precipitate. Therefore, those aluminum compounds should have too strong a reducing ability to $TaCl_5$. An exception among the organoaluminums is vitride, which produced a polymer with a high molecular weight. This can be attributed to its moderate reducing ability and high solubility in nonpolar solvents.

Thus it has been proven that a wide range of organometallics depress polymer degradation in the present polymerization. The requirements for such organometallic cocatalysts appear to be an appropriate reducing or alkylating ability and a function of solubilizing the active species by attaching to it as ligands.

Polymerization by $NbCl_5$-Based Catalysts. The polymerization of 1-phenyl-1-propyne by $NbCl_5$ behaved similarly to that by $TaCl_5$ (Figure 5):[8] Conversion reached 100% after ca. 2 h under the conditions shown in Figure 5. The $\bar{M}_w$ of the polymer formed was as high as ca. 2 × 10^5 just when all the monomer had reacted. Then it dramatically decreased, and the $\bar{M}_w$ after 24 h was no more than several thousand.

Figure 6 shows results for the case that *n*-Bu_4Sn was added at 1:1 molar ratio to $NbCl_5$. The polymerization conditions are the same as in Figure 5. Conversion reached 100% in about 30 min, the reaction being accelerated by the presence of the cocatalyst. The $\bar{M}_w$ of the polymer was practically constant and about 4 × 10^5 irrespective of polymerization time. Thus it is possible to restrain polymer degradation by addition of *n*-Bu_4Sn as in the case of the $TaCl_5$ catalyst.

Cocatalytic effects of various organometallics, which had been useful for the polymerization by $TaCl_5$, were examined (Table VII). All these cocatalysts provided poly(1-phenyl-1-propyne) having fairly high $\bar{M}_w$ values of 1 × 10^5 to 6 × 10^5. It is noteworthy that most of these values are higher than the maximum $\bar{M}_w$ of 2 × 10^5 observed with $NbCl_5$ alone before polymer degradation. When these $NbCl_5$–cocatalyst systems are compared with the corresponding Ta ones, the latter generally achieve higher molecular weights than the former.

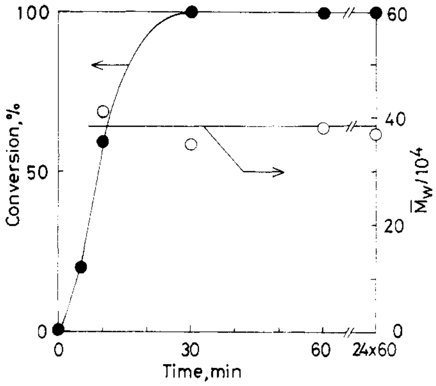


Figure 6. Time dependences of conversion and polymer molecular weight in the polymerization of 1-phenyl-1-propyne by $NbCl_5$–*n*-Bu_4Sn (in toluene, 80 °C, $[M]_0$ = 1.0 M, [Cat.] = [Cocat.] = 20 mM).

Table VII
Effects of Various Organometallic Cocatalysts on the Polymerization of 1-Phenyl-1-propyne by $NbCl_5$[a]

Cocat.	convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
none	100	81	4.7	2.2
n-BuLi	100	100	530	190
9BBN[c]	100	100	140	63
vitride[d]	100	100	600	270
Et_3SiH[e]	100	100	350	130
n-Bu_4Sn	100	93	370	130
Ph_3Bi	100	100	300	120

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 1.0 M, [Cat.] = [Cocat.] = 20 mM. [b] Determined by GPC. [c] 9BBN = 9-borabicyclo[3.3.1]nonane. [d] Vitride: sodium bis(2-methoxyethoxy)aluminum hydride. [e] [Cocat.] = 40 mM.

Discussion

The following three effects of cocatalysts were observed in the polymerization of 1-phenyl-1-propyne by $TaCl_5$ and $NbCl_5$: (i) Polymerization is accelerated. (ii) Degradation of the polymer formed is restrained. (iii) The molecular weight of the polymer becomes higher than the maximum molecular weight attained without a cocatalyst.

It is inferred that organometallic cocatalysts reduce $TaCl_5$ and $NbCl_5$ to form active species, on which moieties of the cocatalysts remain as ligands. Effect (i) should be due to either the increase in the number of active species or the activation of active species, though it cannot be concluded which is the cause.

The present polymer degradation is thought to occur by reaction of double bonds on the polymer chain with Ta- or Nb-containing species. A probable reason for effect (ii) is that, owing to the steric effect of the cocatalyst moieties working as ligands, polymers cannot coordinate to the active species and therefore do not undergo degradation.

In conclusion, it has been proven that use of suitable cocatalysts inhibits polymer degradation in the polymerization of 1-phenyl-1-propyne by $TaCl_5$ and $NbCl_5$. Thus a facile method for synthesizing high-molecular-weight poly(1-phenyl-1-propyne)[13] ($\bar{M}_w$ = 1 × 10^5 to 3 × 10^6) has been established. The reaction mechanism of the polymer degradation is now being studied.

Acknowledgment. Part of this work was supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture (No. 59119005).

Registry No. $TaCl_5$, 7721-01-9; Me_4Sn, 594-27-4; Et_4Si, 631-36-7; Bu_3SnH, 688-73-3; Bu_3SnCl, 1461-22-9; Ph_3SnCl, 639-58-7; Ph_3SiH, 789-25-3; Ph_4Sn, 595-90-4; Ph_3Sb, 603-36-1; BuLi, 109-72-8; *t*-BuLi, 594-19-4; Ph_3B, 960-71-4; $NbCl_5$, 10026-12-7; Bu_4Sn, 1461-25-2; Et_3SiH, 617-86-7; Ph_3Bi, 603-33-8; 9BBN, 280-64-8; poly(1-phenyl-1-propyne), 53621-07-1; sodium bis(2-methoxyethoxy)aluminum hydride, 22722-98-1.

References and Notes

(1) Part 18 of "Polymerization of Phenylacetylenes". For part 17, see ref 2.
(2) Masuda, T.; Takahashi, T.; Higashimura, T. *Macromolecules* **1985,** *18,* 311.
(3) Woon, P. S.; Farona, M. F. *J. Polym. Sci., Polym. Chem. Ed.* **1974,** *12,* 1749.
(4) Sasaki, N.; Masuda, T.; Higashimura, T. *Macromolecules* **1976,** *9,* 664.
(5) For a review, see: Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984,** *17,* 51.
(6) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981,** *14,* 233.
(7) Masuda, T.; Takahashi, T.; Higashimura, T. *J. Chem. Soc., Chem. Commun.* **1982,** 1297.
(8) The time course for intrinsic viscosity was reported.[2] Here the time–$\bar{M}_w$ relationship is shown to help understand the present degradation.
(9) Since the time when 100% conversion is reached is more or less irreproducible owing to trace amounts of water in the system, it is not necessarily easy to prepare a high-molecular-weight poly(1-phenyl-1-propyne) with $TaCl_5$ alone.
(10) Higashimura, T.; Deng, Y.-X.; Masuda, T. *Macromolecules* **1982,** *15,* 234.
(11) Masuda, T.; Yamagata, M.; Higashimura, T. *Macromolecules* **1984,** *17,* 126.
(12) Cotton F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 1275.
(13) See ref 2 for the structure and unique properties of poly(1-phenyl-1-propyne).

Aqueous Polymerization of Acrylamide Initiated with the Permanganate–L-Serine Redox System

U. D. N. Bajpai* and A. K. Bajpai

Department of Post-Graduate Studies and Research in Chemistry, Rani Durgavati Vishwavidyalaya, Jabalpur 482 001, India. *Received September 17, 1984*

ABSTRACT: The effect of various parameters, salts, organic solvents, and temperature on the rate of polymerization of acrylamide initiated by permanganate–L-serine, a new redox system, has kinetically been studied in an inert atmosphere of nitrogen at 35 ± 0.2 °C. Variation in molecular weight of polyacrylamide at varying initial concentration of monomer has also been studied.

Introduction

L-Serine has been used as a reductant in kinetic studies of reduction of Ce(IV), Fenton's reagent, and chloramine-T,[1-3] but its use as an activator in radical polymerization has not been investigated so far. In the present study it is being used, for the first time, as an activator in the polymerization of acrylamide, with potassium permanganate as a catalyst. L-Serine itself finds applications as a vulcanizing accelerator for diene rubber and as a chemical modifier for silk and wool fibers. We have studied in our laboratory permanganate–L-cysteine[4] and permanganate–glycine[5] initiated polymerization of acrylamide. In the same series, we are reporting the results of permanganate–L-serine initiated polymerization of acrylamide.

Experimental Section

Acrylamide was recrystallized twice from methanol (AR) followed by drying under vacuum. Potassium permanganate used was BDH (AnalaR) grade, and its solution was prepared by a standard method.[6] All solutions were prepared in double-distilled water. The apparatus and procedure employed were identical with those used by Misra et al.[7] in which the kinetics of polymerization was followed by estimating the rate of consumption of monomer.

The molecular weight of polyacrylamide was determined by viscometry with Suen's equation[8]

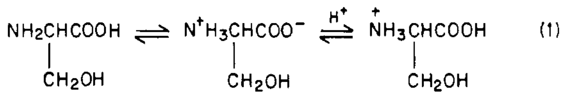
$$[\eta]_{spc} = 6.8 \times 10^{-4} M^{0.66}$$

Results and Discussion

Mechanism. The free radicals, which are responsible for the initiation of polymerization, are produced by the redox reaction between L-serine and potassium permanganate. A plausible mechanism suggested for the present study may be outlined as follows:

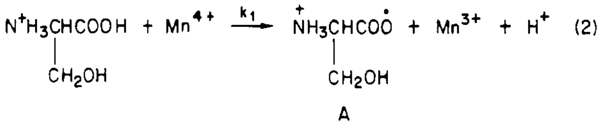
(a) Formation of Free Radicals

In general, L-serine exists predominantly as the protonated species in acidic media according to the equation

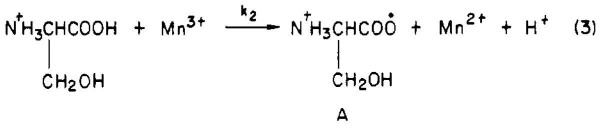


$$\underset{\displaystyle CH_2OH}{NH_2CHCOOH} \rightleftharpoons \underset{\displaystyle CH_2OH}{N^+H_3CHCOO^-} \overset{H^+}{\rightleftharpoons} \underset{\displaystyle CH_2OH}{\overset{+}{N}H_3CHCOOH} \quad (1)$$

In permanganate-containing redox systems, first the permanganate reacts with acrylamide to produce manganese dioxide, which in acidic medium combines with protonated L-serine to yield free radicals A and B (eq 2–4).



$$\underset{\displaystyle CH_2OH}{N^+H_3CHCOOH} + Mn^{4+} \xrightarrow{k_1} \underset{\substack{\displaystyle CH_2OH \\ \displaystyle A}}{\overset{+}{N}H_3CHCO\dot{O}} + Mn^{3+} + H^+ \quad (2)$$



$$\underset{\displaystyle CH_2OH}{\overset{+}{N}H_3CHCOOH} + Mn^{3+} \xrightarrow{k_2} \underset{\substack{\displaystyle CH_2OH \\ \displaystyle A}}{\overset{+}{N}H_3CHCO\dot{O}} + Mn^{2+} + H^+ \quad (3)$$

The MnO_2-controlled initiation (eq 2) has been confirmed by the addition of fresh MnO_2 to the reaction medium, which increases the initial rate of polymerization and maximum conversion as well.

The free radical A produced above now decomposes as follows:

$$A \xrightarrow[\text{fast}]{k_3} \underset{B}{N^+H_3\dot{C}HCH_2OH} + CO_2 \quad (4)$$