Polymerization of Acetylene Derivatives by Transition Metal Alkoxides

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The polymerization of acetylene and its derivatives by various transition metal catalysts were extensively studied.[1-5] Especially W- and Mo-based catalyst systems are very effective for the polymerization of some acetylene monomers.[6,7] In recent years, we reported the polymerization of mono-, and di-substituted acetylenes and the cyclopolymerization of nonconjugated diynes by transition metal-based catalysts.[8-10]

Transition metal alkoxides such as $Mo(OEt)_5$, $Ta(O-t-Bu)_5$, $Nb(O-t-Bu)_5$ have not been used for the polymerization of acetylene derivatives. To our knowledge, $Mo(OEt)_5/Al_2O_3/SiO_2$,[11] $Mo(OEt)_2Cl_3/Et_3B$,[12] $Mo(OEt)_2Cl_3/Me_2Al_2Cl_3$,[13] WO $(OPh)_4/AlCl_3$ (or $EtAlCl_2$),[14] $W(OPh)_6/MeAlCl_2$ were used only for olefin metathesis reaction.

We now report the very interesting results, the high catalytic activity of transition metal alkoxides for the polymerization of some acetylene derivatives.

$Mo(OEt)_5$, $Ta(O-t-Bu)_5$, $Nb(O-t-Bu)_5$ (High Purity Chemicals) were used as received. Propargyl bromide, propargyl chloride, and propargyl alcohol (Aldrich Chemicals) were dried with appropriate drying agent and distilled. Dipropargyl ether and methyl propargyl ether was prepared as described in our previous papers.[10,15] All catalyst system preparation and polymerization procedures were carried out under dry nitrogen atmosphere.[6]

Table 1 shows the results for the polymerization of propagyl chloride by transition metal-based catalysts. $Mo(OEt)_5$-based catalyst system are very effective for this polymerization. On the other hand, $Ta(O-t-Bu)_5$ and $Nb(O-t-Bu)_5$ catalyst systems did not show any catalytic activity.

Table 2 shows the polymerization results of various acetylene derivatives by $Mo(OEt)_5$-based catalysts. $Mo(OEt)_5$ alone shows a considerable amount of catalytic activity for the polymerization of most acetylene derivatives. This high catalytic activity of $Mo(OEt)_5$ alone for the polymerization of acetylene derivatives is very interesting phenonmena though the polymerization mechanism is not fully understood. In our another work,[17] it was found that the polymerization of propargyl alcohol by $MoCl_5$ is explosively proceeded to give a quantative yield of poly (propargyl alcohol). In that case, the active catalytic intermediate was assumed to be molybdenum alkoxides. And also $Mo(OEt)_5$ shows a high catalytic activity for the polymerization of vinyl monomers such as N-vinylcarbazole and indene.[18] Organoaluminum compounds ($EtAlCl_2$, Et_3Al) were used as cocatalysts for the polymerization of propargyl

Table 1. Polymerization of Propargyl Chloride by Transition Metal-Based Catalysts[a]

Exp. No.	Catalyst system[b] (mole ratio)	Polymer yield[c](%)
1	$Mo(OEt)_5$	51
2	$Mo(OEt)_5/EtAlCl_2(1/2)$	64
3	$Mo(OEt)_5/Et_3Al(1/4)$	40
4	$MoCl_5$	30
5	$MoCl_5/Ph_3Bi(1/2)$	5
6	$Ta(O-t-Bu)_5$	0
7	$Ta(O-t-Bu)_5/Et_3Al(1/4)$	0
8	$Ta(O-t-Bu)_5/EtAlCl_2(1/2)$	0
9	$Nb(O-t-Bu)_5$	0
10	$Nb(O-t-Bu)_5/EtAlCl_2$	0

[a]Polymerization was carried out at 60℃ for 24 hrs in chlorobenzene. Initial monomer concentration ($[M]_o$) and monomer to catalyst mole ratio were 1 M and 50, respectively. [b] Mixtures of catalyst and cocatalyst solution were aged at 30℃ for 5 min before use. [c]Methanol-insoluble polymer.

Table 2. Polymerization of Acetylene Derivatives by $Mo(OEt)_5$-Based Catalysts[a]

Exp. No	HC≡C−R R	Catalyst system[b] (mole ratio)	Polymer yield[c](%)
1	CH_2Cl	$Mo(OEt)_5$	51
2	CH_2Cl	$Mo(OEt)_5/EtAlCl_2(1/2)$	64
3	CH_2Cl	$Mo(OEt)_5/Et_3Al(1/4)$	40
4	CH_2Br	$Mo(OEt)_5$	20
5	CH_2OH	$Mo(OEt)_5$	42
6	CH_2OCH_3	$Mo(OEt)_5$	5
7	$CH_2OCH_2C≡CH$	$Mo(OEt)_5$	47

[a]Polymerization was carried out at 60℃ for 24 hrs in chlorobenzene. Initial monomer concentration ($[M]_o$) and monomer to catalyst mole ratio were 1 M and 50, respectively. [b]Mixtures of catalyst and cocatalyst solution were aged at 30℃ for 5 min before use. [c]Methanol-insoluble polymer.

chloride by $Mo(OEt)_5$. $EtAlCl_2$ alone shows some cocatalytic activity. $Mo(OEt)_5$ was also effective for the cyclopolymerization of nonconjugated diynes such as dipropargyl ether and dipropargyl sulfide. The resulting polymers were mostly insoluble in organic solvents as like with those prepared by other transition metal catalysts.[3,16] This insolubility of propargyl-based polymers is assumed to be due to the crosslinking of polymer main chain by active allyl protons.

From this work, we reported the interesting catalytic activity of $Mo(OEt)_5$ for the polymerization of acetylene derivatives. More detailed studies on the polymerization mechanism and the application of this catalyst are in progress.

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Hydrolysis of p-Nitrophenylacetate in Micellar Solution by N,N'-Dichloroisocyanuric Acid Sodium Salts (DCI)

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As a mimic system of enzyme reaction and as a model system of destruction of nerve agents, the hydrolysis reaction of p-nitrophenylacetate (PNPA) or p-nitrophenyl-diphenyl-phosphate (PNPDPP) in micellar or microemulsion system has been extensively investigated.[1]

However, the hydrolysis of PNPA catalyzed by a N-chloro compound has not yet been investigated. We now report some interesting results in the hydrolysis reactions of PNPA by N,N'-dichloroisocyanuric acid sodium salts (DCI) in micellar phase (Table 1). In the nonmicellar phase, DCI gave a 240-fold rate enhancement for the hydrolysis of PNPA over the system without DCI, which means that DCI itself catalyzes the hydrolysis reaction. The degree of the catalyzing effect of DCI was even larger than that of CTABr or 16-OH micellar system. In the micellar system without DCI, 16-OH showed a slightly higher reactivity than CTABr. This result

Table 1. Rate Constants for the Hydrolysis Reaction of PNPA with N,N'-Dichloroisocyanuric Acid Sodium Salts (DCI)[a]

Surfactant	Catalyst	k_1 (s^{-1})	k_2 (s^{-1})	k_1^{cat} $(1, s^{-1}, mol^{-1})$	k_1/k_0
CTABr[b]	DCI	5.1×10^{-2}	1.1×10^{-2}	42.5	2040
16-OH[b]	DCI	1.1×10^{-2}	2.2×10^{-3}	9.2	440
CTACl	DCI	7.6×10^{-3}		6.3	300
none	DCI	6.1×10^{-3}		5.1	240
16-OH	none	6.7×10^{-4}			27
CTABr	none	1.0×10^{-4}			4
none	none	2.5×10^{-5}			1

[a]Condition : 0.05 M phosphate buffer, pH 8.0, 25±0.1℃, [DCI]= 1.2×10^{-3} M, [PNPA]=4×10^{-5} M, [Surfactant]=4×10^{-3} M. Calculated by pseudo first-order kinetics for the release of p-nitrophenolate ion, monitored at 400 nm. Reproducibilities of the rate constants are $< \pm 5\%$. [b]Calculated by series first-order kinetics equation.[2]

X⁺: Halogen species
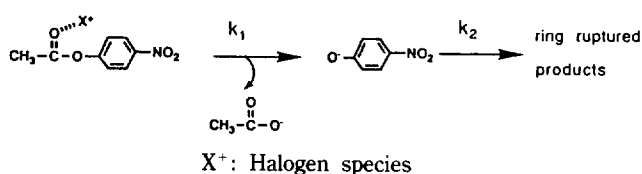
Scheme 1.

was due to the hydroxy functional group of 16-OH.[2]

However, when DCI was used in the micellar system CTABr revealed superior results in the hydrolysis of PNPA than 16-OH did. In CTABr and 16-OH micellar system, the hydrolysis product, p-nitrophenolate was rapidly transformed to other unknown compounds which did not have λ_{max} at 400 nm. It was supposed that the series of decomposition reactions of p-nitrophenolate would occur very rapidly.[4,5] As a result, the hydrolysis reaction of PNPA in CTABr and 16-OH micellar solution showed a typical series first-order kinetics (Scheme 1).

On the other hand, the same reaction condition in CTACl micellar solution did not give typical series first-order kinetics, but simple first-order kinetics. The decay rate of p-nitrophenolate was almost ignorable within 20 min. Moreover, the rate for the hydrolysis reaction of PNPA was 6.7 times slower than in CTABr and even comparable with that of nonmicellar DCI. This means that the counter ions should play an important role in the hydrolysis of PNPA as well as in the breakdown of p-nitrophenolate. As far as we know, this will be the first report that demonstrates the importance of the counter ion of surfactant in catalytic reactions of micellar system.

When DCI was added in CTABr micellar solution, strong absorbance appeared at 264 nm, which was supposed to be the absorbance of Br_3^- ion (λ_{max}, lit[6] 266 nm, ε, 35000 M⁻¹ cm⁻¹). The formation of Br_3^- ion[7] can be easily conjectured if the reaction between DCI and bromide ion yielded BrCl (Scheme 2), which are equilibrated with various bromine species according to the following equations.[8] The bromine species such as BrCl or Br_3^- ion were known to be more reactive than N-chloro compounds in various oxidation reac-