Vinyl Polymerization by Copper—Isonitrile System

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ABSTRACT: New catalyst systems of Cu_2O , $\text{Cu}(\text{acac})_2$ and metallic copper in combination with isonitrile were found for the polymerizations of acrylonitrile, methacrylonitrile, and acrylate. Addition of an active methylene compound to the Cu_2O —isonitrile system increased the catalyst activity. A mechanism of anionic polymerization induced by organocopper—isonitrile complex is proposed. The active methylene compound was assumed to play the major role in increasing the rate of formation of organocopper—isonitrile complex which is responsible for the initiation. The results of the copolymerizations of acrylonitrile with methyl methacrylate and with acrylate are taken to suggest the specific coordination of acrylonitrile onto copper.

KEY WORDS Organocopper / Polymerization / Copolymerization / Acrylonitrile / Coordination / Active Methylene Compounds / Isonitrile / Cuprous Oxide / Copper Metal / Copper Acetylacetonate /

The present paper describes a new catalyst system of the Cu_2O -isonitrile complex for the polymerization of vinyl monomers, especially acrylonitrile. Recently, the catalytic characteristics of the Cu_2O -isonitrile system have been explored for several synthetic reactions. For example, this system catalyzes the Michael-type addition,¹ in which the specific catalyst activity upon addition to acrylonitrile has been demonstrated. Furthermore, acrylonitrile and acrylate are dimerized by this system in the presence of *tert*-butanol and acetonitrile (eq 1).² In the absence of these protic solvents, acrylonitrile is polymerized (eq 2).

This paper characterizes the catalyst behavior of the Cu_2O —isonitrile system for the polymerization of vinyl compounds. As the isonitrile component, *tert*-butyl isocyanide (*t*-BuNC) was employed.

RESULTS AND DISCUSSION

Table I shows that Cu_2O , $\text{Cu}(\text{acac})_2$, and metallic copper in combination with *t*-BuNC cause the polymerization of acrylonitrile. Without the isonitrile component, these copper species did not initiate the acrylonitrile polymerization. The catalyst activity is thus ascribed to complexes between the copper species and isonitrile. The coordination of isonitrile to copper has been demonstrated by the shift of the $\nu_{\text{N}\equiv\text{C}}$ band in the Cu_2O —isonitrile and Cu —isonitrile systems.³ The formation of a soluble complex between metallic copper and isonitrile

Table I. Polymerization of acrylonitrile by copper—isonitrile systems^a

Copper component	Polymerization time, hr	Conversion, %
Cu ₂ O	4.5	31.5
Cu(acac) ₂	8	23.1
Cu	4.5	5.1
CuCl	8	0
CuI	8	0
CuO	8	0
CuCl ₂	8	0

^a Bulk polymerization at 80°C; Cu component, 0.2 mmol; *t*-BuNC, 10 mmol; acrylonitrile, 76 mmol.

Table II. Polymerization of vinyl compounds by the binary system of Cu_2O — $t\text{-BuNC}$ ^a

Monomer	Polymerization time, hr	Conversion, %	Mol wt of polymer ^b
Acrylonitrile	15	100	3350
	4.5	31.5	7700
Methacrylonitrile	4.5	91.4	—
	3	78.6	6640
Methyl acrylate	15	15.9	2390
Methyl methacrylate	15	11.7	23000
Styrene	15	8.9	23800

^a Bulk polymerization at 80°C; Cu_2O , 0.2 mmol; $t\text{-BuNC}$, 10 mmol; monomer, 5.0 ml.

^b Measured by vapor pressure osmometer in DMF.

is of special interest.⁴ The complexization of $\text{Cu}(\text{acac})_2$ with $t\text{-BuNC}$ was also established by IR spectroscopy in the present study: *i.e.*, free $t\text{-BuNC}$ had an absorption due to $\nu_{\text{N}\equiv\text{C}}$ at 2130 cm^{-1} , and the binary system showed an additional band at 2174 cm^{-1} which was assigned to the isonitrile ligand coordinated to $\text{Cu}(\text{acac})_2$. CuCl , CuCl_2 , and CuI are not active either with or without the isonitrile component for the acrylonitrile polymerization, although these copper salts form complexes with isonitrile.

Table II shows some results of the polymerization of several vinyl monomers at 80°C by the Cu_2O — $t\text{-BuNC}$ system. It is demonstrated that the catalyst activity of the binary system is quite specific for the polymerizations of acrylonitrile and methacrylonitrile. The molecular weights of these two polymers, however, were not high. At lower temperatures, *e.g.*, 20°C, acrylonitrile and methacrylonitrile were not polymerized by this binary system. The polymerizations of methyl methacrylate and styrene proceeded quite slowly. It seems very likely that the polymerizations of acrylonitrile, methacrylonitrile, and methyl acrylate have proceeded through an anionic mechanism. This view is supported by several relevant observations which will be discussed in the following part. On the other hand, the polymerizations of methyl methacrylate and styrene in Table II may have proceeded through a radical mechanism, which was caused by heat. Radical polymerization of styrene in the presence of $t\text{-BuNC}$ has been reported by us.⁵

With regard to the interactions of the Cu_2O —isonitrile system with acrylonitrile and with acrylate we have reported the dimerizations of acrylonitrile and acrylate. On the basis of the reaction scheme of these dimerizations, the following reaction may be assumed to form an organocopper complex which initiates the anionic polymerizations of acrylonitrile and acrylate. The enhanced base character of the oxygen of Cu_2O —isonitrile complex may be responsible for the abstraction of α -hydrogen. In conformity with the observations in the catalyst activities of copper—isonitrile complexes, CuCl , CuCl_2 , and CuI did not catalyze the dimerizations of acrylonitrile and acrylate. The mechanism for formation of the organocopper complex in the polymerization of methacrylonitrile is not clear at this moment.

Table III shows an important finding: the addition of the so-called “active methylene compounds” increases the catalyst activity of the Cu_2O —isonitrile system. For example, the

Table III. Polymerization of acrylonitrile by Cu_2O — $t\text{-BuNC}$ (Effect of active methylene compounds^a)

Additive	Solvent	Conversion, %
None	Bulk	0
Bulk	1.5
	Benzene	4.8
	DMF	84.4
Bulk	1.0
	DMF	97.7
DMF	22.8
$\text{CH}_2(\text{CN})_2$	Bulk	0.2
	DMF	23.0
$\text{CH}_2=\text{CHCH}_2\text{CN}$	Bulk	31.2
PhCH_2CN	Bulk	32.1

^a Cu_2O , 0.2 mmol; $t\text{-BuNC}$, 10 mmol; active methylene compound, 10 mmol; acrylonitrile, 76 mmol; solvent, 5.0 ml; 0°C, 3 hr.

Cu₂O—isonitrile system did not induce acrylonitrile polymerization at 0°C. In the presence of an active methylene compound, however, it did induce the acrylonitrile polymerization at this temperature.

The elemental processes of initiation and propagation of the acrylonitrile polymerization by the above catalyst systems are classified as the conjugate addition of organocopper complex to acrylonitrile. The effect for active methylene compounds of increasing the polymerization rate may be explained by their high reactivities towards the Cu_2O —isonitrile system to produce the corresponding organocopper complexes, which are responsible for the initiation of the anionic polymerization. In fact, we⁶ have found that cyclopentadiene easily reacts with Cu_2O in the presence of *t*-BuNC to

produce (*pentahapto*-cyclopentadienyl) (*tert*-butyl isocyanide) copper. A similar reaction was also observed with indene.⁶ The organocopper complexes from cyclopentadiene and indene were found to catalyze the anionic dimerization of crotononitrile and the Michael addition as well as the reaction between the cyclopentadienyl homologues with carbonyl compounds.⁶

With regard to the effects of malononitrile and benzyl cyanide, we have found the 1:1 addition reactions of these active methylene compounds to acrylonitrile and to methyl acrylate in the presence of the Cu_2O —isonitrile system.¹

Rapid reaction of allyl cyanide (2) with the Cu_2O —isonitrile system has also been observed in the dimerization of allyl cyanide to produce 4.

For this dimerization, the intermediacy of the organocopper complexes of **3a** and **3b** has been justified.⁷ Thus, the effect of allyl cyanide in the acylonitrile polymerization by the Cu₂O—isonitrile system may reasonably be ascribed to the rapid formation of an initiating species of organocopper complex.

The systems of bulk polymerization of acrylonitrile by the ternary catalyst systems in Table III were heterogeneous, and the polymer yields were low. In the cases of the catalyst systems consisting of allyl cyanide and of benzyl cyanide, the polymerization systems were homogeneous, and the polymer yield was improved. The systems of solution polymerization in DMF were homogeneous, and the polymer yield was increased.

The acrylonitrile polymerization by the Cu_2O —isonitrile system in the absence of active methylene compound (Table II) required higher reaction temperatures, *e.g.*, 80°C . This is due to the fact that the formation of the initiating species of eq 3 requires higher reaction temperatures than the reactions of the Cu_2O —isonitrile complex with active methylene compounds of Table III.

The nature of the Cu_2O —isonitrile system as initiator was also examined by the copolymerization experiments. Figure 1 and Table IV give the copolymer compositions in the copolymerizations of acrylonitrile with methyl methacrylate (Figure 1) and with methyl acrylate (Table IV). This result is taken to support the anionic mechanism of polymerization by the Cu_2O —

Figure 1. Composition curve for the copolymerization of acrylonitrile (M_1) with methyl methacrylate (M_2): (1) Cu_2O , 0.2 mmol; t -BuNC, 10 mmol; bulk at $80^\circ C$; conversion under 10%; (2) n -BuLi; bulk at $-8^\circ C$; calculated from $r_1=7$, $r_2=0.398$ using Mayo–Lewis equation.

Table IV. Copolymer compositions of acrylonitrile (M_1) with methyl acrylate (M_2)^a

Composition of monomers M_1/M_2 , mmol/mmol	Acrylonitrile unit in copolymer, mole fraction	
	$Cu_2O-t-BuNC^b$	$n-BuLi^c$
75/25	0.907	0.897
50/50	0.814	0.749

^a Each copolymerization conversion was less than 10%.

^b Cu_2O , 0.2 mmol; $t-BuNC$, 10 mmol; bulk, at 80°C.

^c $n-BuLi$, 0.46 mmol; benzene, 1.0 ml; at 0°C.

isonitrile system. The fractions of the acrylonitrile units of the copolymers prepared by the Cu_2O —isonitrile system are a little higher than those prepared by butyllithium. With respect to the catalyst nature of the Cu_2O —isonitrile system, the results of the additions of active hydrogen compounds to α, β -unsaturated carbonyls and nitriles catalyzed by the same system should be mentioned.¹ In the competitive reactions, the reactivity ratio of acrylonitrile/acrylate is raised more by the catalyst of the Cu_2O —isonitrile system than by the typical base catalysts, such as sodium alcoholate and tertiary amine. The increase of the acrylonitrile reactivity was explained by the specific coordination of acrylonitrile to copper. In the polymerization, the coordination of acrylonitrile may be assumed, too. Further studies, however, are necessary for the elucidation of the details of the mechanism.

EXPERIMENTAL

Reagents

The copper compounds were commercial reagents, which were used without further purification. $t-BuNC$ was prepared by the dehydration of N -*tert*-butyl formamide with $POCl_3$ according to Ugi's procedure.⁹ Cyclopentadiene was prepared by the heat cracking of cyclopentadiene dimer at 160–180°C under nitrogen. Commercial reagents of indene, 3-butenonitrile, benzyl cyanide, and malonodinitrile were dried and distilled under nitrogen. Commercial reagent fluorene was used without

further purification. Monomers and solvents were all commercial reagents and were purified by the usual methods and distilled under nitrogen.

Polymerization and Copolymerization Procedures

Polymerization was carried out under nitrogen in a sealed tube. A mixture of 0.2 mmol of Cu_2O , 10.0 mmol of $t-BuNC$, and 5.0 ml of monomer were placed in a sealed tube and the tube was heated at 80°C. After the desired period of polymerization, the polymer solution was dissolved in 20 ml of DMF containing 1 ml of 1 N -HCl aqueous solution, and then the solution was poured into 300 ml of methanol. The precipitated polymer was collected by filtration, washed repeatedly with methanol, and dried *in vacuo*.

Molecular Weight Determination

The osmotic molecular weight was determined in DMF by means of a Hitachi Perkin-Elmer 115 molecular weight apparatus.

Copolymer Composition Determination

The copolymer composition was determined by NMR spectroscopy in $DMSO-d_6$ using a model of 60 Mc Hitachi R-20B (tetramethylsilane as internal standard). The peak area ratio of the peak at τ 7.4 (methoxy proton of methyl acrylate or methyl methacrylate unit) to the multiplet from τ 7.9 to τ 9.1 (methine, methylene and methyl protons, of acrylonitrile and methyl acrylate or methyl methacrylate units) was used for the determination of the composition.

IR spectrum

After 0.5 mmol of $Cu(acac)_2$ and 5.0 mmol of $t-BuNC$ were mixed in 10 ml of benzene and heated to about 60°C for 2 hr, the upper solution was submitted to IR spectroscopy. In addition to the band at 2130 cm^{-1} ($\nu_{N\equiv C}$ of free $t-BuNC$), a new band appeared at 2174 cm^{-1} ; this was attributed to the coordinated species of $t-BuNC$.

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