Vinyl Polymerization by Cyclopentadienylcopper(I) Complexes

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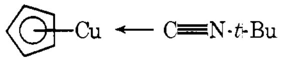
Received October 8, 1974

ABSTRACT: This paper describes the catalyst character of cyclopentadienylcopper(I)–*t*-BuNC complex 1 for vinyl polymerization. Acrylonitrile, methacrylonitrile, methyl methacrylate, and methyl acrylate were polymerized in DMF at 0° by 1 in the presence of a small amount of excess *t*-BuNC. Without excess *t*-BuNC, 1 alone did not show the catalyst activity under these conditions. Upon addition of *t*-BuNC, PPh$_3$ and P(OCH$_3$)$_3$ were found to be effective to activate 1. Copolymerizations of acrylonitrile with methyl methacrylate and with styrene showed that the catalyst system of 1 with *t*-BuNC had a specific preference for acrylonitrile. Coordination of acrylonitrile onto the copper of the catalyst was assumed.

Considerable attention has been paid to organocopper complexes in the fields of organometallic chemistry and organic synthesis, but there are few studies about the catalyst behavior of organocopper toward polymerization of olefinic monomers. The free-radical polymerizations of styrene and acrylonitrile by methylcopper(I) were reported by Bawn, et al., in 1960.[1] Recently Ikariya, et al., reported that an isolated complex of methyl(trialkylphosphine)copper(I) caused the polymerization of acrylonitrile or methyl methacrylate, which was assumed to be a coordination polymerization.[2] In organometallic chemistry, cyclopentadienylcopper(I) complexes, which are among a few examples of stable organocopper complexes, have been studied by several groups of workers.[3] This paper describes some fundamental characters of cyclopentadienylcopper(I) complexes as a catalyst for vinyl polymerization. Previously, vinyl polymerization by the Cu$_2$O–isonitrile system was explored by us,[4] in which organocopper complexes were assumed to be formed *in situ* as the real species of polymerization catalyst. In the present study, cyclopentadienylcopper(I) complexes were isolated and utilized.

Results and Discussion

Vinyl Polymerization by Cyclopentadienylcopper(I) Isonitrile Complex. According to our method,[3g] (η^5-cyclopentadienyl)(*tert*-butyl isocyanide)copper(I) (1), (CPD)-Cu(*t*-BuNC), was prepared from Cu$_2$O, cyclopentadiene, and *t*-BuNC. In the present study, 1 was found to be sublimable, and so, it was purified by sublimation under reduced nitrogen pressure prior to use as a catalyst.



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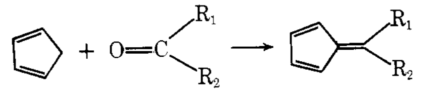
A purified sample of 1 alone did not induce the acrylonitrile polymerization in dimethylformamide (DMF) at 0°. But 1 did induce the acrylonitrile polymerization in the presence of a small excess of *t*-BuNC. A high level of catalyst activity was attained by adding about 50 mol % of excess *t*-BuNC to 1 (Figure 1). This activation by the presence of excess isonitrile is closely related to a similar phenomena in the reaction of cyclopentadiene with carbonyl compounds to produce the corresponding fulvene compounds by a catalyst of 1 (eq 1), *i.e.*, the yield of the fulvene product was much increased when an excess of *t*-BuNC was added in the reaction mixture.[3g] The function of an excess of isonitrile to increase the catalyst reactivity of 1 both in the polymerization and in the fulvene synthesis may be attributed to the increase of electron density of the cyclopentadienyl group by the coordination of isonitrile onto copper. Thus, the nucleophilic reactivity of cyclopentadienyl group is increased. In fact, nmr study showed the upfield shift of the peak due to the cyclopentadienyl protons, from τ 3.75 to 4.21, when 10 times the amount (moles) of *t*-BuNC to 1 was added.



(1)

Table I shows some illustrative results of polymerizations of vinyl monomers by a catalyst of 1 with 100 mol % excess *t*-BuNC. The mole per cents of catalyst to monomer in Table I are between 0.2 and 0.5. The catalytic activity of this system is quite specific for the polymerizations of acrylonitrile, methacrylonitrile, and methyl methacrylate. In the polymerization of methyl acrylate under the same conditions as in Table I, a considerable amount of methanol-soluble polymer of low molecular weight was produced. The production of a low molecular weight polymer of methyl acrylate may be due to frequent chain transfer reaction between the propagating species of the organocopper complex and the α hydrogen of the monomer. The abstraction of such an active hydrogen atom by organocopper isonitrile complex has been observed in several synthetic reactions.[5]

The specificity of the selection of monomers of this catalyst system is quite similar to that observed with the Cu$_2$O–isonitrile system as a catalyst of vinyl polymerization.[4] In the polymerizations with both catalyst systems, the propagating species are organocopper isonitrile complexes, which have high reactivities to the addition to α,β-unsaturated nitrile, carbonyl, and ester.[4–6]

The system of 1 with excess *t*-BuNC induced the acrylonitrile polymerization at temperatures as low as −78° (Table II), which was much more reactive than the Cu$_2$O–isonitrile system. In the polymerization by the Cu$_2$O–isonitrile system, the reaction between monomer and catalyst to produce organocopper complex of the real active species required higher temperature such as 80°.[4]

Table II shows the results of acrylonitrile polymerization by the catalyst systems of 1:1 mixtures of 1 and varions ligand compounds. Three compounds of *t*-BuNC, triphenylphosphine (PPh$_3$), and trimethyl phosphite (P(OCH$_3$)$_3$) were found to be effective to activate 1. In the presence of an equimolar amount of one of these ligand compounds, the acrylonitrile polymerization was caused by 1 even at −78°. The acrylonitrile polymerization by PPh$_3$ alone has been reported by Jaaks, *et al.*,[7] which proceeded much slower at 30°, *i.e.*, a 10% conversion after 1 week. Therefore, it is clear that the organocopper complex is responsible for the catalyst activity under the conditions of the present study.

In the system of 1 with PPh$_3$, the ligand exchange between *t*-BuNC and PPh$_3$ may occur to produce a complex of (CPD)CuPPh$_3$, 2. Some relevant data are given in Table III, in which acrylonitrile was polymerized by 2 with or

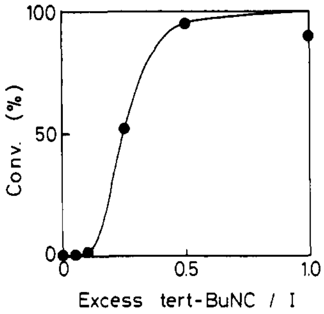


Figure 1. Effect of excess *t*-BuNC on the acrylonitrile polymerization by 1: **1**, 0.20 mmol; AN, 76 mmol; DMF, 15.0 ml; at 0° for 1 hr.

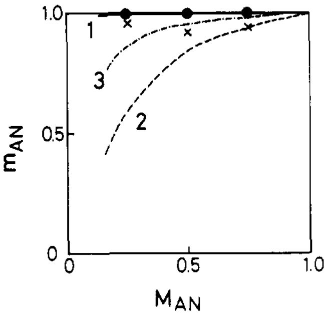


Figure 2. Copolymerization of acrylonitrile (AN) with methyl methacrylate (MMA); curve 1 (—●—), 1 + *t*-BuNC (1:1), −78° in DMF (points X at 0°); curve 2, BuLi, −8° in bulk, calculated from Zutty's data[9] (γ_{AN} = 7, γ_{MMA} = 0.39); curve 3, PhMgBr, −70° in toluene, calculated from Dawan's data[10] (γ_{AN} = 5, γ_{MMA} = 0.03).

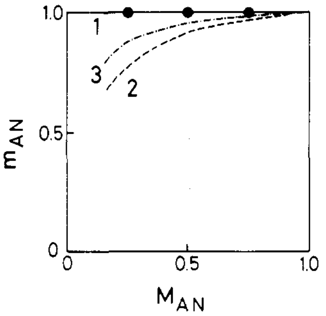


Figure 3. Copolymerization of acrylonitrile (AN) with styrene (ST); Curve 1 (—●—), 1 + *t*-BuNC (1:1), 0° in DMF; curve 2, BuLi, −12° in ether, calculated from Zutty's data[9] (γ_{AN} = 14, γ_{ST} = 0.20); curve 3, PhMgBr, −70-0° in ether–toluene[10] (γ_{AN} = 20.0, γ_{ST} = 0.02).

without excess *t*-BuNC. Here it is shown that excess *t*-BuNC does activate the catalyst of **2** although **2** by itself can cause the acrylonitrile polymerization at a slower rate at 0°.

Pyridine, quinoline, tetrahydrofuran, diglyme, and carbon monoxide were not effective to activate **1**. Carbon monoxide is isoelectronic to isonitrile, but its electron-donating nature as ligand is known to be weaker in comparison with isonitrile because of its good π acceptability.[8]

Copolymerization by (CPD)Cu(*t*-BuNC) and *t*-BuNC. The catalyst character of the system of **1** with *t*-BuNC has been demonstrated by copolymerization experiments. In the copolymerizations of acrylonitrile with methyl methacrylate and with styrene, the copolymer composition curves were obtained as shown respectively in Figures 2 and 3. In both copolymerizations, this organocopper catalyst showed a marked preference for acrylonitrile. The preference is more pronounced in comparison with the literature data with butyllithium and Grignard reagent catalysts in these copolymerizations.

Table I
Polymerization of Vinyl Monomers by 1 and *t*-BuNC (1:1)[a]

Monomers	Polymerization time	Conv, %	Polymer mol wt
Acrylonitrile	20 min	86.2	36,600
Methacrylonitrile	20 min	54.2	10,730
Methyl methacrylate	40 min	51.3	25,600
Styrene	72 hr	0	

[a] **1**, 0.20 mmol; *t*-BuNC, 0.20 mmol; DMF, 5.0 ml; monomer, 5.0 ml; at 0°.

Table II
Acrylonitrile Polymerization by 1 and Various Ligand Compounds[a]

Ligand	Polymerization		Conv,
	Temp, deg C	Time, hr	%
t-BuNC	-78	0.5	5.8
	-78 → 0[b]	1.0	89.4
PPh_3	-78	0.5	85.7
	-78 → 0[b]	1.0	93.7
$P(OCH_3)_3$	-78	0.5	7.0
	-78 → 0[b]	1.0	97.0
Pyridine	0	1.0	0.3
Quinoline	0	1.0	0.2
THF	0	1.0	0.1
Diglyme	0	1.0	0.1
CO	-78	0.5	0
O_2	-78	0.5	0

[a] **1**, 0.20 mmol; ligand compound, 0.20 mmol; acrylonitrile, 76 mmol; DMF, 15.0 ml. [b] Monomer and catalyst system was mixed at −78°, and polymerized at 0°.

Table III
Acrylonitrile Polymerization by 2 (Effect of *t*-BuNC[a])

Catalyst	Polymerization time	Conv, %
2	6 hr	14
2 + *t*-BuNC (1:1)	20 min	71

[a] Catalyst, 0.20 mmol; acrylonitrile, 76 mmol; DMF, 5.0 ml; at 0°.

The polymer products in the polymerization of a mixture of acrylonitrile and styrene by the organocopper catalyst were found to consist exclusively of the acrylonitrile unit, *i.e.*, the nmr spectra of the polymer products showed no peak which would be assigned to the phenyl protons of the styrene unit. In the copolymerization of acrylonitrile with methyl methacrylate, the content of the acrylonitrile unit was higher with the organocopper catalyst than with butyllithium and Grignard reagent catalysts. A similar specificity was observed also with the Cu_2O–isonitrile system.[4] The reaction conditions of the reference data are not exactly identical, but the preference of the organocopper catalyst for acrylonitrile is well demonstrated in Figures 2 and 3.

Furthermore, the results of the addition of active methylene compounds to α,β-unsaturated carbonyl and nitrile compounds by the catalyst of the Cu_2O–isonitrile system[5b] are to be mentioned here. In a series of experiments of competitive addition of an active methylene compound to an equimolar mixture of acrylonitrile and acrylate, the reactivity ratio of acrylonitrile to acrylate with the Cu_2O–isonitrile catalyst was much higher than the ratios with the usual base catalysts such as sodium alcoholate and tertiary amine. The specific increase of the acrylonitrile reactivity in the copolymerization and in the addition by the copper catalyst may be due to the specific coordination of acrylonitrile to copper probably through the cyano group.

Experimental Section

Reagents. Vinyl monomers were commercial reagents, which were purified by usual procedures and distilled under nitrogen before use. DMF was a commercial reagent and was dried over CaH_2 and distilled under nitrogen. *t*-BuNC was prepared according to Ugi's procedure.[11] PPh_3 was a commercial reagent, which was used without purification. $P(OCH_3)_3$ was a commercial reagent and was distilled under nitrogen.

Isolation and Purification of Cyclopentadienylcopper Complexes. 1 was prepared from cyclopentadiene, Cu_2O, and *t*-BuNC according to our method[3g] and then purified by recrystallization using a combination of ether (solvent) and pentane (nonsolvent) at −20° followed by sublimation at 60° under a reduced nitrogen pressure of 0.3 mm. 2 was prepared from cyclopentadiene, *t*-BuOCu, and PPh_3 according to our method.[12]

Polymerization and Copolymerization. Polymerization was carried out under nitrogen in a sealed test tube. In the case of addition of CO or O_2, the test tube was equipped with a self-sealing cap, and gas was introduced through a syringe. After polymerization, the polymer solution was poured into a mixture of CH_3OH and aqueous HCl solution. The product polymer was filtered, washed with CH_3OH, and dried *in vacuo.* Molecular weight was determined in DMF by means of a Hitachi Perkin-Elmer 115. Copolymerization was stopped at conversions below 10%. Copolymer composition was determined by nmr spectroscopy in d_6-DMSO. In the spectra of the product polymers of the acrylonitrile–styrene copolymerization by the 1–*t*-BuNC system, no peak which would be attributed to the phenyl hydrogens of the styrene unit was observed. The composition of acrylonitrile–methyl methacrylate copolymer was determined based on the area ratio of the peak at τ 7.4 (the methoxy hydrogens of methacrylate unit) to the multiplet from τ 7.9 to 9.1 (total of the methine, methylene, and methyl hydrogens of both units).

Nmr Measurement. The nmr spectrum was measured using a 60-MHz Hitachi R-20B spectrometer.

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The Spontaneous Homopolymerization of Vinylidene Cyanide and Unsaturated Ethers on Mixing the Two Monomers, and the Formation of 1:1 Alternating Copolymers in the Presence of a Free Radical Initiator

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ABSTRACT: The reaction of vinylidene cyanide with the unsaturated ethers *p*-dioxene, dihydropyran, ethyl vinyl ether, isopropyl vinyl ether, and ketene diethyl acetal in a variety of solvents at 25° spontaneously afforded poly(vinylidene cyanide), the cycloaddition products 7,7-dicyano-2,5-dioxabicyclo[4.2.0]octane and 8,8-dicyano-2-oxabicyclo[4.2.0]octane, the 1,1-dicyano-2-alkoxycyclobutanes, and 1,1-diethoxy-2,2,4,4-tetracyanocyclohexane, respectively, and, with the exception of *p*-dioxene, homopolymers of the unsaturated ethers. In the presence of AIBN at 80°, alternating copolymers were obtained in addition to the homopolymers and the cycloaddition products, supporting the involvement of donor–acceptor complexes.

Studies of the polymerization of electron-donating vinyl monomers, especially *N*-vinylcarbazole[1] and vinyl ethers,[2] initiated by electron acceptors which are unable to undergo polymerization themselves, support a mechanism of initiation involving an initial donor–acceptor complex which generates a radical cation from the donor vinyl monomer and a radical anion from the acceptor molecule by a one-electron "T-class" reaction.[3] The radical ions have been implicated both in the formation of the 2 + 2 cycloaddition product and in the formation of a polymer from the donor vinyl monomer by a cationic propagation reaction. Only limited information on the reactions of electron-donating vinyl monomers with electron-accepting vinyl monomers, both of which can undergo polymerization, is available. The report[4] that mixing certain vinyl ethers with vinylidene cyanide gave homopolymers of each of these two types of monomers, and that these polymerizations were occurring by the simultaneous cationic polymerization of the vinyl ether and the anionic polymerization of the vinylidene cyanide, prompted the further investigation of this type of polymerization reaction. Vinylidene cyanide is a strong electron acceptor which homopolymerizes by anionic propagation, but polymerizes only very slowly in the presence of a radical initiator.[4,5] Alkyl vinyl ethers, dihydropyran, *p*-dioxene, and ketene diethyl acetal were chosen as the donor vinyl monomers to be used in this study. With