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A New Radical Initiator of the Binary System of Cupric Methoxide and Carbon Monoxide

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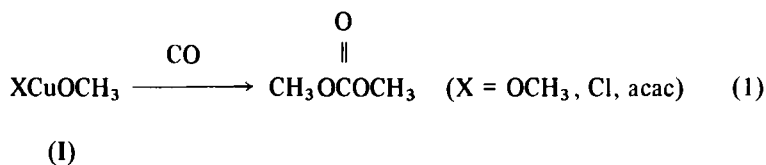
SUMMARY

Under carbon monoxide pressure, cupric alkoxides such as cupric methoxide, $\text{Cu}(\text{OCH}_3)_2$, and cupric acetylacetonate methoxide, $\text{Cu}(\text{acac})(\text{OCH}_3)$, initiate the polymerization of vinyl monomers. The microstructure of polybutadiene and the composition of styrene-methacrylate copolymer by these catalyst systems have indicated a free radical mechanism. The mechanism of the initiation was examined by the end group of product polymer and the analysis of the reaction between the catalyst components. Reduction of $\text{Cu}(\text{OCH}_3)_2$ and $\text{Cu}(\text{acac})(\text{OCH}_3)$ with carbon monoxide to $\text{Cu}(\text{OCH}_3)$ and $\text{Cu}(\text{acac})$, respectively, was responsible for the initiating activity. The decomposition of these unstable cuprous species produces methoxyl and acetylacetonyl radicals which initiate the polymerization.

INTRODUCTION

This paper is concerned with a new radical initiator of the binary system of cupric alkoxide and carbon monoxide. In a previous paper [1] an interesting carbonylation reaction of copper compound was described. Cupric methoxides, namely, cupric dimethoxide (I, $\text{X} = \text{OCH}_3$), cupric chloride methoxide (I, $\text{X} = \text{Cl}$), and cupric acetylacetonate methoxide (I, $\text{X} = \text{acac}$),

react with carbon monoxide (CO) to produce dimethyl carbonate in high yields.



It has now been found that the binary systems of $\text{Cu}(\text{OCH}_3)_2\text{-CO}$ and $\text{Cu}(\text{acac})(\text{OCH}_3)\text{-CO}$ induce the polymerizations of vinyl monomers. This paper describes the results of the polymerization by this initiating system and the mechanism of radical polymerization as well as the nature of the initiating species.

EXPERIMENTAL

Materials

Monomers. Styrene was purified by washing with sodium hydroxide and sodium bisulfite aqueous solutions, successively, drying over calcium chloride, and distilling under reduced nitrogen pressure. Methyl methacrylate was shaken repeatedly with dilute alkali and water, dried over calcium chloride, and distilled under reduced nitrogen pressure. Butadiene gas (pure grade) was passed through the potassium hydroxide and Drierite columns, condensed, and stored over molecular sieves.

Solvents. Dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) were dried by refluxing over calcium hydride and then fractionally distilled. Pyridine was dried by refluxing over potassium hydroxide and calcium hydride and fractionally distilled.

Initiators. $\text{Cu}(\text{OCH}_3)_2$ and CuClOCH_3 were synthesized from CuCl_2 and LiOCH_3 in methanol [2]. $\text{Cu}(\text{acac})\text{OCH}_3$ was obtained by the reaction of $\text{Cu}(\text{acac})_2$ and potassium hydroxide in methanol [3]. $\text{Cu}(\text{acac})_2$ and di-*tert*-butyl peroxide (DTBP) were commercial reagents which were used directly. Carbon monoxide gas was a commercial reagent.

Procedures

Polymerizations were made under nitrogen. Cupric methoxide and the

solvent were placed in a 50-ml stainless steel tube to which monomer was added. Styrene was added at room temperature and butadiene was condensed in the reaction tube at -78°C . Carbon monoxide was then compressed at the temperature of monomer addition and the tube was closed. The content of the tube was heated with shaking. After a given time, the polymerization mixture was dissolved in benzene and the benzene solution was centrifugated and poured into methanol to precipitate the polymer. The microstructure of polybutadiene was analyzed by IR spectrum according to Morero's method [4].

RESULTS AND DISCUSSION

Results of the styrene polymerization initiated by cupric methoxide-CO systems are given in Table 1. The role of CO as an essential component of catalyst system was clearly demonstrated. At 75°C , $\text{Cu}(\text{OCH}_3)_2$ or $\text{Cu}(\text{acac})\text{OCH}_3$ alone did not initiate the styrene polymerization. At 100°C , they caused a slight polymerization, probably due to thermal polymerization. Under the pressure of CO, however, they became active in the polymerization of styrene. A high pressure of CO was not needed; similar activity was observed under CO pressures as low as 10 kg/cm^2 . In addition, the activity of the $\text{Cu}(\text{OCH}_3)_2$ species prepared in situ from CuCl_2 and NaOCH_3 did not differ from that of the isolated species. The combination of cupric chloride methoxide, $\text{Cu}^{\text{II}}(\text{OCH}_3)\text{Cl}$, and CO did not show any noticeable initiation activity. As will be discussed later, these observations are important from the mechanistic point of view. The IR spectrum analysis showed that the polymeric product by the $\text{Cu}(\text{OCH}_3)_2$ -CO system was polystyrene which did not contain any detectable amount of ketonic unit due to carbon monoxide.

The polymerization of butadiene was also performed by the cupric methoxides-CO systems, where similar characteristics were observed (Table 2). Combinations of $\text{Cu}(\text{OCH}_3)_2$ -CO and $\text{Cu}(\text{acac})(\text{OCH}_3)$ -CO were effective for the initiation of butadiene polymerization although the $\text{Cu}(\text{OCH}_3)\text{Cl}$ -CO system was inactive. Polymer products obtained by the $\text{Cu}(\text{acac})(\text{OCH}_3)$ -CO system were sticky semisolids and were easily soluble in benzene. On the other hand, the polymers by the $\text{Cu}(\text{OCH}_3)_2$ -CO system were gummy and were partly soluble in benzene. The IR spectrum of the polymer by the $\text{Cu}(\text{OCH}_3)_2$ -CO system showed no absorption due to the ketonic unit of carbon monoxide.

The mechanism of free-radical polymerization has been established by the microstructure of the butadiene polymer and the composition of the

Table 1. Styrene(ST) Polymerization by Cupric Methoxide-CO System^a

Cupric methoxide	Cupric methoxide	CO (kg/cm ²)	Solvent (mmoles)	Conversion (%)
Polymerization in pyridine at 75°C				
Cu(OCH ₃) ₂	1.12	—	11.2	0
Cu(OCH ₃) ₂	0.99	70	9.9	9
Cu(OCH ₃) ₂	0.88	70	8.8	7
CuCl ₂ ^c	0.90	60	4.5	6
NaOCH ₃	1.80			
Cu(acac)(OCH ₃)	0.56	—	5.0	0
Cu(acac)(OCH ₃)	0.84	70	8.4	3
Cu(acac)(OCH ₃)	0.82	10	8.2	2
Polymerization in DMSO at 100°C				
_d	_d	_d	4.4	8
Cu(OCH ₃) ₂	0.80	—	8.0	16
Cu(OCH ₃) ₂	0.77	70	7.7	52
Cu(OCH ₃) ₂	0.87	70	8.7	0 ^b
Cu(acac)(OCH ₃)	0.72	—	7.2	14
Cu(acac)(OCH ₃)	0.83	70	8.3	64
Cu(OCH ₃)Cl	0.91	60	9.1	2
Cu(acac) ₂	0.83	70	8.3	0


^aST/cupric methoxide = 100 (mole ratio); time, 5 hr.

^bHydroquinone (0.87 mmole) was added.

^cCu(OCH₃)₂ prepared in situ in pyridine at room temp for 30 min from CuCl₂ and NaOCH₃.

^dPolymerization without any added catalyst.

Table 2. Polymerization of Butadiene by Cupric Methoxide-CO System^a

Cupric methoxide	Cupric methoxide (mmoles)	(kg/cm ²)	Solvent	(mmoles)	Conversion (%)
Cu(OCH ₃) ₂	1.11	—	DMSO	56	3
Cu(OCH ₃) ₂	1.37	65	DMSO	69	16
Cu(OCH ₃) ₂	1.51	60	THF	76	12
Cu(acac)(OCH ₃)	1.01	—	DMSO	51	2
Cu(acac)(OCH ₃)	1.65	65	DMSO	83	52
Cu(acac)(OCH ₃)	1.50	65		15	19
Cu(OCH ₃)Cl	1.27	65	DMSO	64	0.6
Cu(OCH ₃)Cl	1.20	60	THF	60	0
(t-BuO) ₂	1.00	—	DMSO	50	6

^aButadiene/cupric methoxide = 100 (mole ratio); temp, 100°C; time, 20 hr.

styrene-methacrylate copolymer. The microstructures of butadiene polymers produced by the Cu(OCH₃)₂-CO and Cu(acac)(OCH₃)-CO systems were almost the same as the structure of the sample formed by an authentic free-radical initiator (Table 3).

The copolymer from equimolar amounts of styrene and methyl methacrylate by the binary initiator systems of the present study consisted of the equimolar amounts of the styrene and methacrylate units (Table 4). The copolymer composition was characteristic of free-radical polymerization.

The IR spectrum of polybutadiene produced by the Cu(acac)(OCH₃)-CO system was quite informative as to the nature of the initiating species. A band due to the carbonyl group was observed at 1718 cm⁻¹, which was reasonably ascribed to the acetylacetyl group but not to the unit of carbon monoxide because the spectra of butadiene polymers produced by the Cu(OCH₃)₂-CO and (t-BuO)₂-CO systems showed no absorption in this region. When the butadiene polymer by the Cu(acac)(OCH₃)-CO system was treated with 2,4-dinitrophenylhydrazine in an acidic medium, the band at 1718 cm⁻¹ disappeared and a new band due to the hydrazone group appeared at 1618 cm⁻¹. The presence of the acetylacetyl group in polymer

Table 3. Microstructure of Polybutadiene by Cupric Methoxide-CO System^a

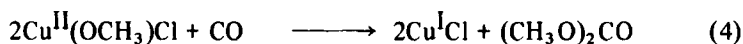
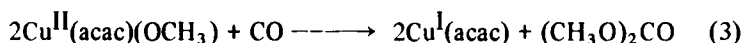
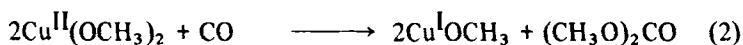
Initiator	Microstructure (%)		
	cis-1,4-	trans-1,4-	1,2-
Cu(OCH ₃) ₂ -CO ^b	33.2	45.5	21.3
Cu(acac)(OCH ₃)-CO	27.6	50.8	21.6
(t-BuO) ₂	27.4	50.9	21.7

^aButadiene polymers were obtained in DMSO solvent in Table 2.

^bBenzene-soluble part of polymer was analyzed.

may be taken to suggest the initiation by the acetylacetylonyl radical from the catalyst system. Another possibility for the incorporation of the acetylacetylonyl group is the radical chain transfer reaction between the growing chain and the acetylacetonate ligand of the catalyst. The second possibility, however, is less likely because the polymerization of butadiene by (t-BuO)₂ initiation in the presence of Cu(acac)(OCH₃) has produced a polymer having no carbonyl band.

The elucidation of the reaction of cupric alkoxide with carbon monoxide is important for understanding the mechanism of the formation of the initiating species. Our previous study [1] has shown that the cupric alkoxide is reduced by carbon monoxide to the corresponding cuprous species with the production of dialkyl carbonate. The following equations indicate the reductions of Cu(OCH₃)₂, Cu(acac)(OCH₃), and Cu(OCH₃)Cl.



Among the three cuprous compounds, cuprous methoxide [5] and acetylacetonate [6] are known to be unstable, whereas cuprous chloride is stable. The formation of these unstable cuprous species is responsible for initiation. The decomposition of cuprous methoxide will produce metallic copper and the methoxyl radical, and the decomposition of cuprous acetylacetonate yields metallic copper and the acetylacetylonyl radical.

Table 4. Copolymerization of Styrene (ST) with Methyl Methacrylate (MMA) by Cupric Methoxide-CO System^a

Cupric methoxide	Cupric methoxide (mmole)	ST (mmoles)	MMA (mmoles)	Solvent DMSO (mmoles)	Conversion (%)	Composition of copolymer, ^b ST unit/MMA unit (mole ratio)
Cu(OCH ₃) ₂	0.96	48.0	48.0	84	5	0.94
Cu(acac)(OCH ₃)	0.92	46.2	46.3	77	6	1.01

^aTemp, 80°C; time, 2.5 ~ 3 hr; CO, 70 kg/cm².

^bDetermined by elemental analysis of copolymer.

The formation of metallic copper was actually observed in the polymerization by these binary catalysts. The presence of the acetylacetyl group in the butadiene polymer by the $\text{Cu}(\text{acac})(\text{OCH}_3)\text{-CO}$ system was thus rationalized. In addition, dimethyl carbonate was detected by GLPC analysis in the distillate of reduced pressure distillation of the polymerization system. The $\text{Cu}(\text{OCH}_3)\text{Cl-CO}$ system is inactive because cuprous chloride is stable and does not generate any free radical.

In summary, $\text{Cu}(\text{OCH}_3)_2$ and $\text{Cu}(\text{acac})(\text{OCH}_3)$ under CO pressure initiate the free-radical polymerization of vinyl monomers. The production of unstable species of $\text{Cu}(\text{OCH}_3)$ and $\text{Cu}(\text{acac})$ by the reduction of cupric alkoxides with carbon monoxide is responsible for the initiation. The decomposition of these cuprous species generates methoxyl and acetylacetyl radicals, respectively. A feature of the new radical initiator of the present study lies in the fact that unstable initiating species are formed in situ by the reaction with carbon monoxide.

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