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### Metal-Containing Initiator Systems. XXIX. Selective Initiation of Vinyl Polymerizations with Cobaltocene

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## **Metal-Containing Initiator Systems. XXIX. Selective Initiation of Vinyl Polymerizations with Cobaltocene**

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### **ABSTRACT**

The polymerizations of acrylonitrile (AN), acrolein (AL), butadiene (BD), and isobutyl vinyl ether (IBVE) with cobaltocene were investigated. It was found that both AN and AL could polymerize in dimethyl sulfoxide through a coordination mechanism, but AN and BD polymerized by a radical mechanism in the presence of some organic halides, such as carbon tetrachloride, benzyl bromide, and allyl bromide. The initiator system of cobaltocene and organic halide also induced cationic polymerization of IBVE. On the basis of the results obtained, a mechanism for the selective initiation of polymerization is proposed and discussed.

## INTRODUCTION

In previous papers [1-5] of this series, it was found that some metal-containing initiator systems, reduced nickel/organic halides [1, 2], metal acetylacetonate/organic halide [3], and bisbenzenchromium or ferrocene/organic halide [4, 5] could selectively induce radical and ionic polymerizations, depending on the reactivities of vinyl monomers used. Since we recently found similar behavior for cobaltocene [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co] initiator, the present paper will describe the results regarding selective polymerization of vinyl monomers.

## EXPERIMENTAL

### Materials

Cobaltocene was synthesized according to Wilkinson's method [6] and purified by sublimation. Organic halides used in this study were purified by distillation from the commercially available reagents. Acrylonitrile (AN), acrolein (AL), butadiene (BD), and isobutyl vinyl ether (IBVE) were distilled in a stream of nitrogen just before use. The other reagents, such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), toluene, and methanol, were commercial materials used after distillation and purification.

### Polymerization Procedure

The polymerizations and copolymerizations were carried out in a sealed tube without light under shaking in a thermostat maintained at a given temperature. After polymerization, the tube was removed from the thermostat and cooled in a Dry Ice-methanol bath. Then this tube was opened and its contents poured into a large amount of methanol (or diethyl ether in the case of AL) to precipitate the polymer. The resulting polymer was filtered, washed several times with precipitant, and then dried under vacuum.

### Analyses of Polymers

The intrinsic viscosity [ $\eta$ ] of poly-AN was measured in as the dilute DMF solution at 25°C, and the number-average molecular weight  $\bar{M}_n$  was calculated from Eq. (1) [7]:

$$[\eta] = 57.4 \times 10^{-5} \overline{M}_n^{0.73} \quad (1)$$

The microstructure of the poly-BD was determined from its infra-red spectrum according to the method of Morero [8]. The composition of the copolymers of AN was determined from their nitrogen contents.

## RESULTS AND DISCUSSION

### Polymerizations of AN and AL with $(C_5H_5)_2Co$

The results of polymerizations of AN and AL with  $(C_5H_5)_2Co$  are shown in Table 1.

The polymerization systems of both monomers changed from black-violet to black-brown during the polymerization. Table 1 shows that AN could easily polymerize with  $(C_5H_5)_2Co$  in DMSO to give polymer with low intrinsic viscosity. The rates of polymerization increased with increasing polymerization temperature. The resulting polymers were pale yellow-colored powders, soluble in DMSO, DMF, and acetone but insoluble in carbon tetrachloride, chloroform, acetonitrile, and nitrobenzene. Under similar conditions, AL quite rapidly polymerized with  $(C_5H_5)_2Co$  even at 30°C in DMSO and in DMF, and the polymers obtained were white powders.

The effects of solvents and additives on the polymerization of AN with  $(C_5H_5)_2Co$  were also investigated. As can be also seen from Table 1, AN polymerized both in DMSO and in DMF, but is hardly polymerized in toluene. Thus the polymerization activity was found to change according to the solvent used in the following order: DMSO > DMF > toluene. However, when a small amount of ethylenediamine (ED) dipyriddy (Dipy), triphenylphosphine (PPH<sub>3</sub>), or diethylenetetramine (DETA) which could coordinate with  $(C_5H_5)_2Co$  was added, the activity in toluene was in almost agreement with that in the absence of these additives.

In a previous paper [9], these additives were found to show a marked accelerating effect on the polymerization of AN with  $(C_5H_5)_2Ni$ , unlike the case with  $(C_5H_5)_2Co$ . This reason for the difference in behavior seems that either  $(C_5H_5)Co$  rapidly reacts with these additives having a bidentate ligand such as amine or forms a stable complex, because the activity of  $(C_5H_5)_2Co$  is higher than that of  $(C_5H_5)_2Ni$ .

To clarify this polymerization further, a study of the kinetics of the polymerization of AN with  $(C_5H_5)_2Co$  was performed. The time-conversion relations obtained in DMSO at 50-80°C are shown in Fig. 1.

TABLE 1. Polymerization of Acrylonitrile (AN) and Acrolein (AL) with  $(C_5H_5)_2Co^a$ 

Monomer	Solvent	Additive		Temperature (°C)	Time (hr)	Yield (%) <sup>b</sup>
		Type	Concn. (mole/ liter)			
AN	DMSO	—		60	12	37.2(0.12)
AN	DMSO	—		70	12	58.8
AN	DMSO	—		80	12	81.8
AN	DMSO	—		90	12	93.7(0.07)
AN	DMF	—		70	12	9.2
AN	Toluene	—		70	15	1.2
AN	Toluene	ED	0.09	70	15	3.1(0.05)
AN	Toluene	Dipy	0.04	70	15	3.5
AN	Toluene	PPh <sub>3</sub>	0.04	70	15	1.8
AN	Toluene	DETA	0.09	70	15	3.3
AL	DMSO	—		30	0.25	100
AL	DMF	—		30	0.25	90

<sup>a</sup>Polymerization conditions:  $[(C_5H_5)_2Co] = 2 \times 10^{-3}$  mole/liter;  $[AN] = 7.6$  mole/liter;  $[AL] = 7.5$  mole/liter in solvent.

<sup>b</sup>Values in parentheses indicate values of intrinsic viscosity (dl/g in DMF).

The yield of the polymer increases linearly with time at every temperature. From the Arrhenius plots of the logarithms of polymerization rates with reciprocal polymerization temperatures, as shown in Fig. 2, the overall activation energy was obtained as 9.3 kcal/mole. This value is considerably lower than that of ordinary radical polymerization.

In order to investigate the polymerization mechanism of AN with  $(C_5H_5)_2Co$ , the polymerizations of AN with methyl methacrylate (MMA), styrene (St), and AL were carried out in DMSO at 70°C. The monomer-copolymer composition curves obtained are shown in Fig. 3, from which

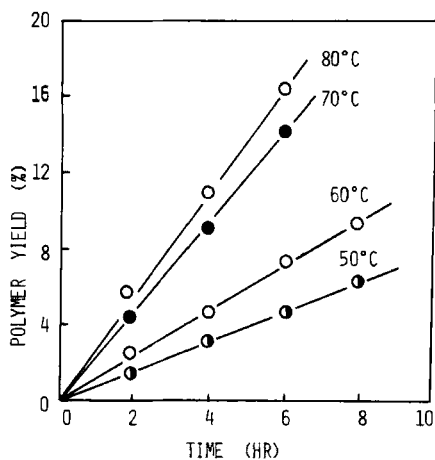


FIG. 1. Effects of temperatures on the polymerization of AN with  $(C_5H_5)_2Co$ ;  $[AN] = 7.6$  mole/liter;  $[(C_5H_5)_2Co] = 2 \times 10^{-3}$  mole/liter in DMSO.

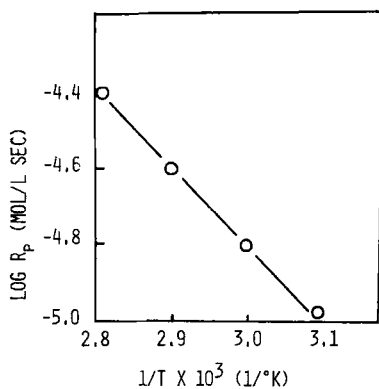


FIG. 2. Arrhenius plot of  $\log R_p$  with  $1/T$ :  $[AN] = 7.6$  mole/liter;  $[(C_5H_5)_2Co] = 2 \times 10^{-3}$  mole/liter in DMSO.

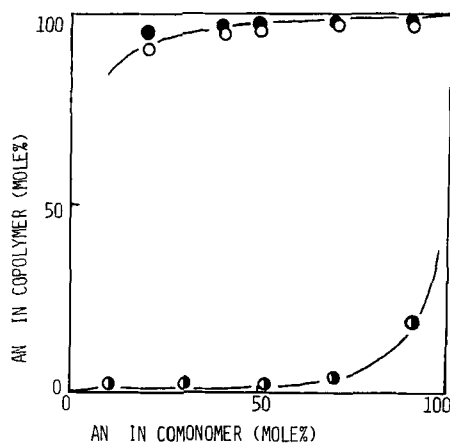


FIG. 3. Copolymer composition curves in the copolymerizations of AN with various monomers: (●) AN-MMA; (○) AN-St; (●) AN-AL.  $[(C_5H_5)_2Co] = 2 \times 10^{-3}$  mole/liter in DMSO at  $70^\circ C$ .

it is clear that in both AN-MMA and AN-St systems, the homopolymer of AN is obtained almost exclusively, independent of the monomer feed. However, the copolymerization of AN with AL is found to give the homopolymer of AL, probably due to the higher reactivity of AL toward  $(C_5H_5)_2Co$  than AN. These results strongly indicate that the polymerization of AN and of AL in DMSO is performed through a coordination mechanism, not ordinary radical and anionic mechanism. Similar results were also found for the polymerization of AN with  $(C_6H_6)_2Cr$  and  $(C_5H_5)_2Ni$  [9, 10].

The IR spectra of the copolymers obtained by these copolymerizations are shown in Fig. 4. As can be seen from this figure, only the absorption band due to poly-AN is observed in the copolymers obtained from the AN-MMA and AN-St systems, but that due to poly-AL is found in the copolymers obtained from the AN-AL system. Therefore, the polymerization of AN (and also of AL) with  $(C_5H_5)_2Co$  in DMSO seems to proceed via a coordination mechanism involving a  $\pi-\sigma$  rearrangement of the  $\pi$ -complex formed initially between  $(C_5H_5)_2Co$  and AN monomer [Eq. (2)].

A similar mechanism was proposed for the polymerizations of AN and AL with some metal  $\pi$ -complexes [9, 10], and the detailed results will be described in a subsequent paper.

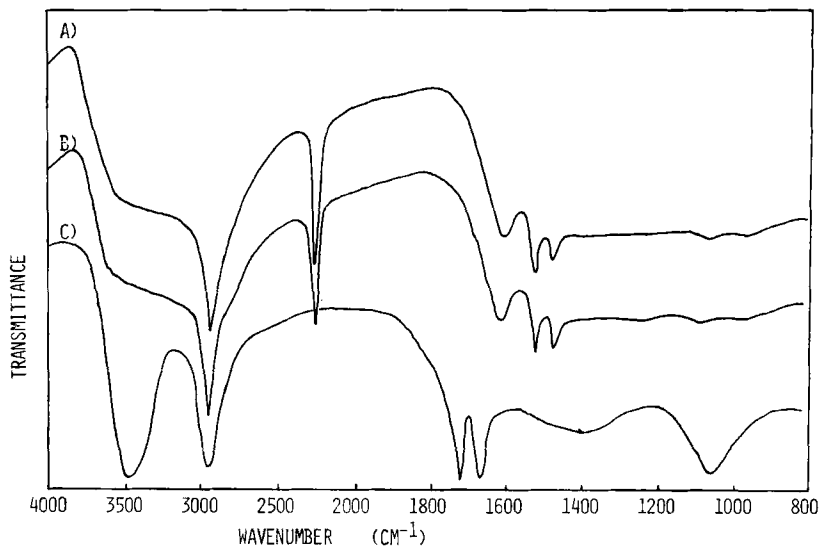
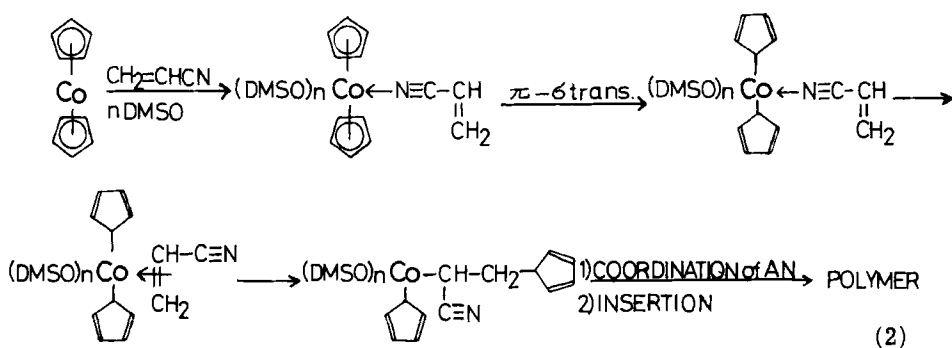


FIG. 4. Infrared spectra of the copolymers obtained from: (A) AN-MMA; (B) AN-St; (C) AN-AL systems.



#### Polymerization of Vinyl Monomers with (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co-Alkyl Halides (RX)

The results of polymerization of AN with (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co-RX systems are shown in Table 2. AN polymerizes in the absence of RX to give low molecular weight polymer, but in the presence of halides such as



TABLE 2. Polymerization of Acrylonitrile with  $(C_5H_5)_2Co$  at  $70^\circ C^a$ 

Solvent	Halide		Time (hr)	Yield (%)	$[\eta]$ (dl/g)	$\bar{M}_n$
	Type	Concn. (mole/ liter)				
Toluene	$CCl_4$	0.1	18	5.4		
Toluene	$CHCl_3$	0.1	18	0		
Toluene	$C_6H_5CH_2Cl$	0.08	18	0		
Toluene	$C_6H_5CH_2Br$	0.08	18	1.2		
Toluene	$CH_2=CHCH_2Cl$	0.1	18	0		
Toluene	$CH_2=CHCH_2Br$	0.1	18	0.6		
Toluene	None	-	18	1.2		
DMF	$CCl_4$	0.1	7	14.3	1.87	62,000
DMF	$C_6H_5CH_2Br$	0.1	18	11.0	4.90	240,000
DMF	$CH_2=CHCH_2Br$	0.1	18	10.3		
DMF	$CH_2=CHCH_2Cl$	0.1	16	2.2		
DMF	None	-	18	6.4	0.07	710

<sup>a</sup>Polymerization conditions:  $[(C_5H_5)_2Co] = 2 \times 10^{-3}$  mole/liter;  
 $[AN] = 7.6$  mole/liter.

$CCl_4$ ,  $C_6H_5CH_2Br$ , and  $CH_2=CHCH_2Br$  the polymerization of AN is accelerated much more in DMF than in toluene. The activity of RX in DMF decreases in the following order:  $CCl_4 > C_6H_5CH_2Br > CH_2=CHCH_2Br > CH_2=CHCH_2Cl > C_6H_5CH_2Cl$ . This order was in almost agreement with that observed with  $(C_6H_5)_2Cr$  [4],  $(C_5H_5)_2Fe$  [4], and  $(C_5H_5)_2Ni$  [5]. It is noted that all of the resulting polymers obtained are white powders of high molecular weight ( $10^5$ - $10^6$ ). From these results, it seems that these polymerizations with  $(C_5H_5)_2Co$  in the presence of RX proceed through a mechanism other than the coordination mechanism described above.

In order to clarify the mechanism of polymerization with the  $(C_5H_5)_2Co$ -RX system, the copolymerization of AN and St with a  $(C_5H_5)_2Co$ - $CCl_4$  system was carried out. The results are shown in

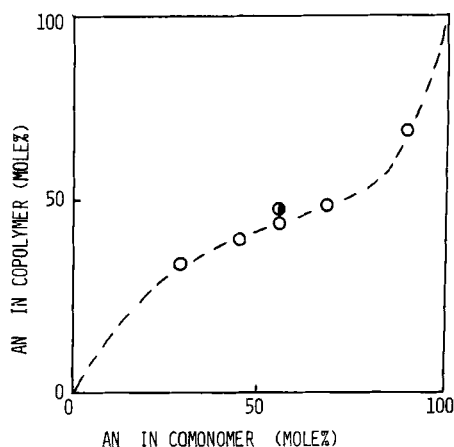
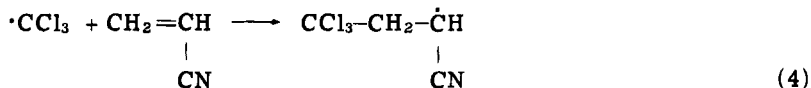
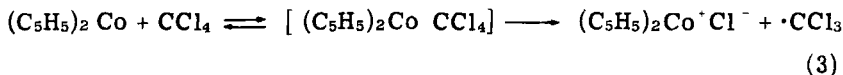


FIG. 5. Copolymerization of St ( $M_1$ ) with AN ( $M_2$ ) by  $(C_5H_5)_2Co-CCl_4$  system: (○) in toluene; (●) in DMF. Copolymerization conditions:  $[(C_5H_5)_2Co] = 2 \times 10^{-3}$  mole/liter;  $[CCl_4] = 1 \times 10^{-1}$  mole/liter at  $70^\circ C$ .

Fig. 5. The observed composition curve is in agreement with that obtained with the ordinary radical polymerization. The experimental points obtained in DMF lie on this composition curve. Therefore, the mechanism in the presence of RX is found to be that of radical polymerization proposed by Otsu and Kubota et al. [4] for the initiation by the  $(C_5H_5)_2Fe-RX$  system [Eqs. (3) and (4)]. Namely,  $(C_5H_5)_2Co$  can initially form a complex with RX like  $CCl_4$ , and one electron-transfer from  $(C_5H_5)_2Co$  to  $CCl_4$  occurs to produce the trichloromethyl radical, which can initiate the radical polymerization [Eqs. (3) and (4)].



A similar mechanism was proposed from the results of product analysis by Hagihara et al. [11].

TABLE 3. Polymerization of Butadiene (BD) and Isobutyl Vinyl Ether (IBVE) with  $(C_5H_5)_2Co^a$ 

Monomer	Halide (RX)	Temperature (°C)	Time (hr)	Yield (%) <sup>b</sup>	Microstructure (%)		
					1,2	cis-1,4	trans-1,4
BD <sup>c</sup>	-	90	48	3.4	26.7	24.6	48.9
BD	-	90	48	0	-	-	-
BD	CCl <sub>4</sub>	90	48	23.7(0.33)	18.0	38.1	43.9
BD	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	90	48	16.7(0.45)	25.0	38.4	36.6
BD	CH <sub>2</sub> I <sub>2</sub>	90	48	12.5(0.42)	25.4	35.8	38.8
IBVE	-	60	18	0	-	-	-
IBVE	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	60	18	2.5	-	-	-
IBVE	-	60	38	0 <sup>d</sup>	-	-	-
IBVE	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	60	38	21.2 <sup>d</sup>	-	-	-

<sup>a</sup>Polymerization conditions:  $[(C_5H_5)_2Co] = 2 \times 10^{-2}$ ,  $[BD] = 6.18$  mole/liter.

<sup>b</sup>Values in parentheses indicate intrinsic viscosity.

<sup>c</sup>Thermal polymerization in the absence of  $(C_5H_5)_2Co$ .

<sup>d</sup>Results obtained by using  $(C_6H_5)_2Cr$  in  $CH_3NO_2$ .

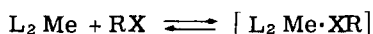
Polymerizations of BD and IBVE

The results of polymerization of BD and IBVE with  $(C_5H_5)_2Co-RX$  systems are shown in Table 3. Although little evidence of thermal polymerization of BD is observed, the addition of  $(C_5H_5)_2Co$  inhibits this polymerization. However, the presence of RX with  $(C_5H_5)_2Co$  catalyst is accelerated the polymerization. The resulting polymers are colorless, and their microstructures are almost identical to those obtained from thermal and radical polymerizations. This result seems to suggest that these polymerizations proceed via a radical mechanism.

From Table 3, however, it is also found that IBVE polymerizes with the  $(C_5H_5)_2Co-C_6H_5CH_2Br$  system, similarly to polymerization of the  $(C_6H_6)_2Cr-C_6H_5CH_2Br$  system [5]. Since IBVE can polymerize only with cationic catalyst, it is considered that the cationic polymerization of IBVE is induced by this catalyst system.

Selective Initiation Mechanism with  $(C_5H_5)_2Co$  in the Presence of RX

As described above, it was found that the binary systems of  $(C_5H_5)_2Co$  and RX served as a selective initiator which induced both radical polymerization of AN and cationic polymerization of IBVE. In addition,  $(C_5H_5)_2Co$  was also induced the coordination polymerization of AN and AL in the absence of RX. The radical polymerization of AN seems to be initiate from the complex I, from which the initiating radical is produced via either unimolecular one-electron transfer of I from metal to RX or bimolecular reaction of I with the monomer (M) used [Eqs. (5) and (6)]:



I



or



where Me and L stand for metal and cyclopentadienyl ligand, respectively. The formation of a charge-transfer complex like I was deduced

spectroscopically by Tsubakiyama [12], who found complex formation between ferrocene and carbon tetrachloride.

On the other hand, the initiation of cationic polymerization of IBVE by these systems is expected to occur by a cation produced through either unimolecular dissociation of I or bimolecular reaction [Eqs. (7) and (8)].



or



A similar selective initiation mechanism was also proposed by Razuvaev [13] with the bisarenechromium-RX system, and by Otsu et al. for reduced nickel-RX [2] and bisbenzenechromium-RX systems [5].

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