

AROMATIC AND HETEROCYCLIC NITRILES AND THEIR POLYMERS XVIII. THE POLYMERIZATION KINETICS OF BENZONITRILE CATALYZED BY METAL ACETYLACETONATE

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ABSTRACT

The bulk polymerization of benzonitrile catalyzed by Co (II), Co (III) and Fe (III) acetylacetonate was studied. The results of kinetics study show that the rate of polymerization was proportional to first power of the concentration of catalyst and second power of the concentration of monomer.

INTRODUCTION

Aromatic and heterocyclic dinitriles can be polymerized to form a new kind of crosslinked polymers containing aromatic and heterocyclic ring in the main chain. These polymers possess excellent thermal stability and other thermal performances.

There are two kinds of catalysts used for the polymerization of aromatic nitriles. One is protonic acid such as chlorosulfonic acid^[1,2], p-toluene sulfonic acid^[3]. The other is Lewis acid. When chlorosulfonic acid is used as solvent as well as catalyst, the polymerization rate is high, but the thermal stability of the polymer obtained is not so good. The polymerization of aromatic nitriles using Lewis acid as catalyst has been thoroughly studied in our laboratory^[7-9], the polymer obtained possesses better high temperature properties, but the polymerization rate is not so high for the application, such as composite preparation. Recently, we have reported Lewis acid metal system as catalyst for the polymerization of aromatic nitriles^[10], although the polymerization rate is accelerated, but it is still not high enough. Therefore, to find a more effective catalyst for the polymerization of aromatic nitriles is one of our objects in the research field of polymerization of aromatic and heterocyclic nitriles. It has been reported that some organometallic compounds are effective catalyst for the trimerization of acetylene or 2:1 molar ratio of acetylenes and nitriles to form pyridines^[11]. Therefore, we intend to use some organometallic compounds as catalyst to effect the polymerization of aromatic nitriles. In this paper, some results of polymerization of benzonitrile catalyzed by metal acetylacetonate are presented.

EXPERIMENTAL

Metal acetylacetonates were prepared from acetylacetone and corresponding

metal chloride according to the literature procedure^[12], and purified by sublimation. The elemental analysis data are listed in Table 1.

Table 1 Element analysis of metal acetylacetonate

Mt (acac) _x	C (%)	H (%)	O (%)	C (%)	H (%)	O (%)
	Calculated			Found		
Co (acac) ₃	50.57	5.94	26.95	50.46	5.93	26.76
Co (acac) ₂	46.71	5.49	24.89	46.73	5.45	24.91
Ni (acac) ₂	46.75	5.49	24.91	46.94	5.67	25.34
Fe (acac) ₃	51.01	5.99	27.18	50.99	5.91	—
Cu (acac) ₂	45.88	5.39	24.45	46.10	5.44	24.82

acac : $\text{CH}_3\text{COCH}_2\text{COCH}_3$

Benzonitrile was washed with saturated sodium carbonate solution four times to remove benzoic acid and washed three times with water, then extracted into ether, dried overnight with calcium chloride and the ether was removed by evaporation. Finally, it was distilled on phosphorus pentoxide under reducing pressure. The middle portion was collected (b. p. $190 \pm 1^\circ\text{C}$). This portion was dried with molecular sieve over one week before being used.

The polymerization was carried out in a sealed glass tube under controlled temperature ($\pm 0.5^\circ\text{C}$). The unreacted benzonitrile was measured by weighing method, i.e., the weight loss at 110°C under 666Pa pressure for 32h.

RESULTS AND DISCUSSION

1. Polymerization of benzonitrile catalyzed by organometallic compounds

Three kinds of organometallic compounds are used, they are: (1) metal acetylacetonates, (2) metal carbonyls, and (3) ferrocene. The results of polymerization of benzonitrile catalyzed by three organometallic compounds are listed in Table 2.

Table 2 Some organometallic compounds used as catalyst for polymerization of benzonitrile

Organometallic Compounds	Solubility in benzonitrile		Yield of polymer (%)
	room temp.	270°C	
Co (acac) ₂	+++	+++	55.2
Co (acac) ₃	+++	+++	44.3
Cu (acac) ₂	+	++	8.5*
Ni (acac) ₂	++	+++	38.0*
Fe (acac) ₃	++	+++	13.6*
Pd (acac) ₂	—	—	0
Nd (acac) ₂	—	—	0
Fe (CO) ₅	+++	decomp. —	0
CO ₂ (CO) ₃	+++	decomp. —	0
Rh ₆ (CO) ₁₆	—	—	0
Ferrocene	—	—	0

Molar ratio of catalyst to benzonitrile: 0.02 : 1 Temperature: 270°C ; time: 10h

"+++": easily soluble "++": soluble "+": slightly soluble "—": insoluble

* : Molar ratio of catalyst to benzonitrile : 0.05 : 1

From Table 2, it is indicated that only several metal acetylacetonates have catalytic activity for the polymerization of benzonitrile. Metal carbonyls are decomposed or insoluble at the polymerization temperature. Ferrocene shows no catalytic activity for the polymerization of benzonitrile at 270 °C, too. It is also indicated from the Table 2 that the catalytic efficiency is strongly depended on the solubility of organometallic compounds in benzonitrile.

Lewis acids are widely used as catalyst for the polymerization of aromatic nitriles, the comparison of their catalytic activity with that of metal acetylacetonates are shown in Table 3.

Table 3 Catalyst activity for the polymerization of benzonitrile

Lewis acids ^[6]	Yield (%)	M (acac) _x	Yield (%)
ZnCl ₂	12.5	Co (acac) ₂	66.5
CoCl ₂	10.0	Co (acac) ₃	45.0
CuCl ₂	4.8	Cu (acac) ₂	8.5
ZnCl ₂ /Zn	36.1	Ni (acac) ₂	38.0
CoCl ₂ /Zn	53.2	Fe (acac) ₃	22.5

Temperature: 270 °C time: 10h

Molar ratio of catalyst to benzonitrile: 0.05 : 1

From the data in Table 3, the catalytic activity of some metal acetylacetonates for polymerization of benzonitrile are more effective than that of Lewis acid or Lewis acid-metal.

2. The polymerization kinetics of benzonitrile catalyzed by metal acetylacetonates

The conversion of benzonitrile (molar ratio of catalyst to monomer: 0.02 : 1) was determined at 270 °C catalyzed by Co (acac)₂, Co (acac)₃, and Fe (acac)₃, respectively. The results are shown in Fig.1.

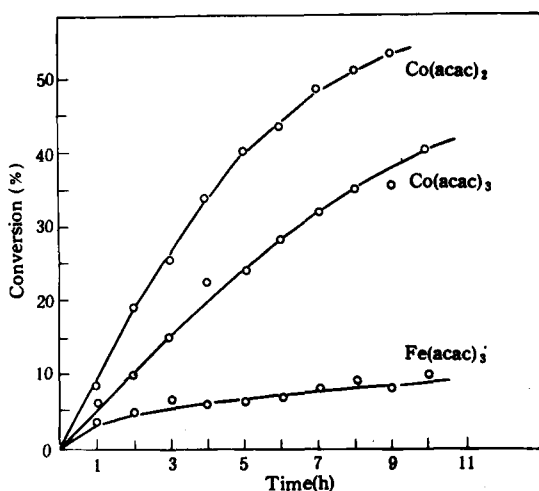


Fig. 1 The conversion of benzonitrile catalyzed by metal acetylacetonates

Polymn. temp.: 270 °C ; [CN]/[M (acac)_x]
= 1/0.02 molar ratio

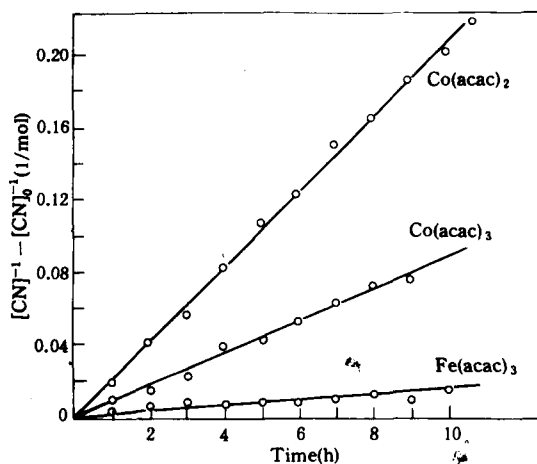


Fig. 2 The relation between $[CN]^{-1} - [CN]_0^{-1}$ and the time of polymerization of benzonitrile catalyzed by metal acetylacetonates

Polymn. Temp.: 270 °C ; [CN]/[M (acac)_x] =
1 : 0.02 molar ratio

The plot of $1/[\text{CN}] - 1/[\text{CN}]_0$ against time is shown in Fig. 2. The result indicates that the rate of polymerization of benzonitrile is proportional to the second power of concentration of benzonitrile (Fig. 2).

The conversion with different concentration of catalyst at 270 °C for a given time was measured, and the results are shown in Fig. 3.

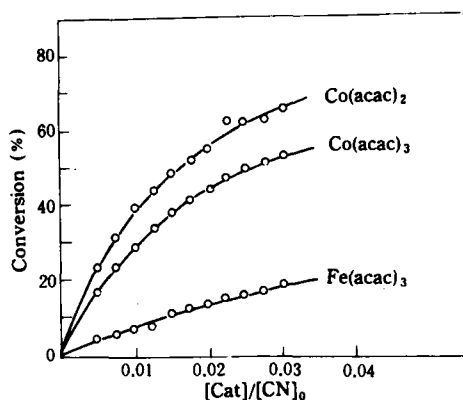


Fig. 3 The conversion of benzonitrile catalyzed by metal acetylacetonates
Polymn. temp.: 270 °C Polymn. time: 10h

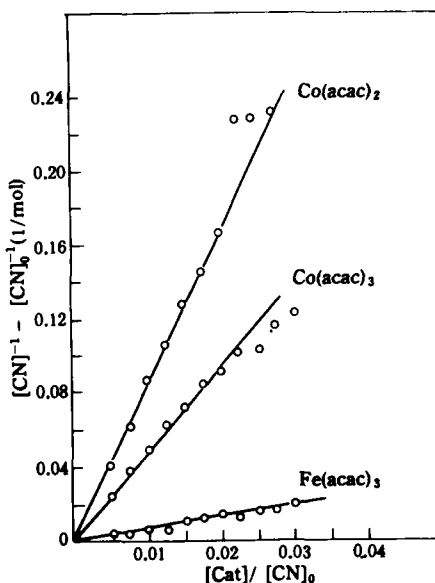


Fig. 4 The relation between $[\text{CN}]^{-1} - [\text{CN}]_0^{-1}$ and the molar ratio of catalyst to monomer
Polymn. temp.: 270 °C; Polymn. time: 10h

The plot of $1/[\text{CN}] - 1/[\text{CN}]_0$ against $M(\text{acac})_x / [\text{CN}]_0$ is shown in Fig. 4. This indicates that the polymerization rate is directly proportional to the concentration of catalyst. Therefore, the polymerization kinetics of benzonitrile catalyzed by metal acetylacetonates can be expressed as follows:

$$V_{\text{polymn}} = -d[\text{CN}]/dt = k' [\text{CN}]^2 = k [\text{Cat}] [\text{CN}]^2 \quad (1)$$

Integrated form is:

$$[\text{CN}]^{-1} - [\text{CN}]_0^{-1} = k' t = kt [\text{Cat}] \quad (2)$$

According to equation(2), the rate constants can be obtained from the slopes of the straight lines in Fig. 2 and Fig. 4, respectively. Table 4 shows that the rate constants are nearly the same. This proves equation (1) being correct for the polymerization of benzonitrile.

Table 4 The polymerization rate constants of benzonitrile catalyzed by metal acetylacetonates

$M(\text{acac})_x$	$k (\text{mol}^{-2} \text{l}^2 \text{h}^{-1})^a$	$k (\text{mol}^{-2} \text{l}^2 \text{h}^{-1})^b$
$\text{Co}(\text{acac})_3$	0.0589	0.0626
$\text{Co}(\text{acac})_2$	0.135	0.110
$\text{Fe}(\text{acac})_3$	0.0120	0.0113

Polymerization temperature: 270 °C

a: from Fig. 2. b: from Fig. 4.

The conversion of polymerization of benzonitrile catalyzed by $\text{Co}(\text{acac})_3$ at different temperatures is shown in Fig. 5.

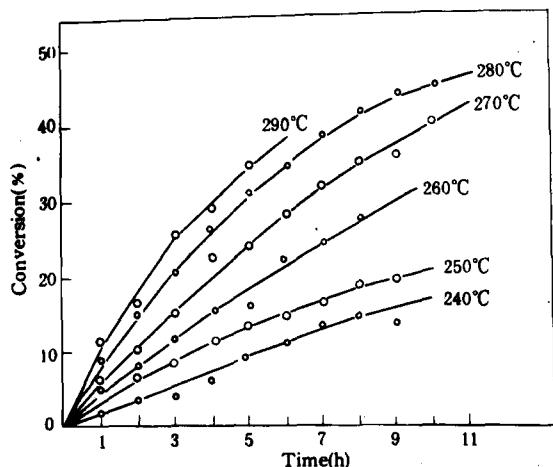


Fig. 5 The polymerization of benzonitrile catalyzed by $\text{Co}(\text{acac})_3$ at different temperatures
 $[\text{CN}]/[\text{Co}(\text{acac})_3] = 1/0.02$ molar Ratio

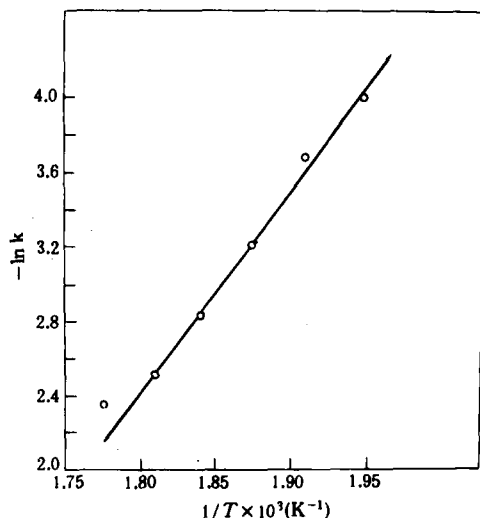
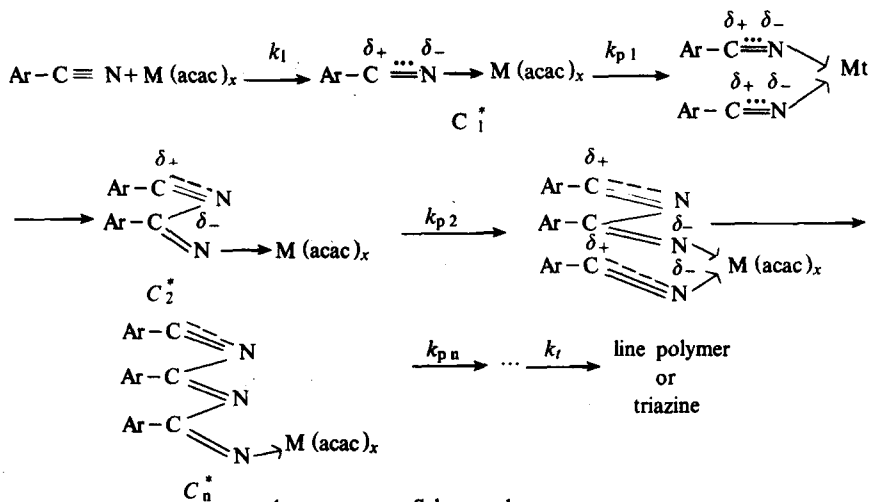


Fig. 6 The relation between $\ln k$ and $1/T$

The rate constants of polymerization calculated by the above mentioned method are: 0.0184, 0.0253, 0.0404, 0.0589, 0.0815, and 0.0962 $\text{L}^2\text{mol}^{-2}\text{h}^{-1}$ at 240, 250, 260, 270, 280, and 290 $^{\circ}\text{C}$, respectively. The activation energy obtained from Arrhenius plot (Fig. 6) is 89.54 KJ/mol and frequency factor is $2.36 \times 10^7 \text{ L}^2 \text{mol}^{-2}\text{h}^{-1}$.

3. Mechanism of the polymerization

Referring to the literatures^[8,11], the following mechanism is proposed for the polymerization of benzonitrile catalyzed by metal acetylacetonate (Scheme 1).



Scheme 1.

In the first step, the active complex (C_1^*) was formed. Rate of the formation can be denoted as follows:

$$R_i = d[C^*]/dt = k_1 [CN] [Cat]$$

After the first active complex is formed, another cyano group coordinates with it, and then addition occurs to form other active complex (C_2^*). Propagation consists of the growth of C_i^* by the successive additions of numbers of nitrile molecules. According to Scheme 1, each addition creates a new active complex, so the rate of propagation is:

$$\begin{aligned} V_{\text{polymn.}} &= - \frac{d[CN]}{dt} = (k_{p1}[C_1^*] + k_{p2}[C_2^*] + \dots + k_{pn}[C_n^*])[CN] \\ &= \sum_{i=1}^n k_{pi}[C_i^*][CN]. \end{aligned}$$

If every new active complex has the same activity then:

$$k_p = k_{p1} = k_{p2} = \dots = k_{pn}.$$

$$[C^*] = [C_1^*] + [C_2^*] + \dots + [C_n^*]$$

So the rate of propagation can be written as follows:

$$V_{\text{polymn.}} = k_p [C^*][CN] \quad (3)$$

where $[C^*]$ is the steady state concentration of active intermediate. According to the rate of active compound produced and reacted, the equation can be got as follows:

$$d[C^*]/dt = k_1 [Cat][CN]$$

$$\text{So } [C^*] = (k_1/k_t) [Cat][CN] = k''[Cat][CN] \quad (4)$$

introducing this equation to the equation (3). The rate of polymerization can be showed as follows:

$$V_{\text{polymn.}} = (k_p k_1/k_t) [Cat][CN]^2 = k [Cat][CN]^2 \quad (5)$$

This is identical with the experimental result [equation (1)].

Keywords:

Benzonitrile; Metal acetylacetonate; Catalyst; Polymerization.

REFERENCES

- [1] Anderson, D. R. and Holovka, J. M., *J. Polym. Sci., A-1*, **1966**, *4*, 1689.
- [2] Копылов В. В. ДАН СССР, **1973**, 207, 610; **1973**, 209, 862.
- [3] Hsu, L. C., ACS symp., **1974**, (4), 145.
- [4] Toland, Jr., W. G., *U. S. P.* 3,060, 179, **1963**.
- [5] Vogel, H. A., *U. S. P.*, 3, 654, 192, **1972**.
- [6] Huang, Z. T. and Ou, Y. C., *Polym. Commun.* (in Chinese), **1978**, (1), 1.
- [7] He, X. H. and Huang, Z. T. *Polym. Commun.* (in Chinese), **1985**, (5), 361.
- [8] Huang, Z. T. and He, X. H.; *Polym. Commun.*, **1985**, (3), 226.
- [9] He, X. H.; Huang, Z. T. and Wang, B. R., *Polym. Commun.*, **1988**, (6), 215.
- [10] Sun, L. Y. and Huang, Z. T., *Chinese J. Polym. Sci.*, **1989**, *7*, 38.
- [11] Boennemann, H.; *Angew. Chem. Intern. Ed.*, **1978**, *17*, 505.
- [12] "Catalysts Handbook" (in Chinese), Chem. Eng. Pub., Beijing, **1982**, p595.