

AROMATIC AND HETEROCYCLIC NITRILES AND THEIR POLYMERS XIX: THE POLYMERIZATION OF SUBSTITUTED BENZONITRILES CATALYZED BY COBALTIC ACETYLACETONATE

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ABSTRACT

The polymerization kinetics of 4,4'-biphenyldicarbonitrile and other substituted benzonitriles catalyzed by cobaltic acetylacetonate was studied. The structure of polymer of different substituted benzonitrile was also determined. It is found that the rate of polymerization and the structure of polymer is greatly affected by the substituent of benzonitriles.

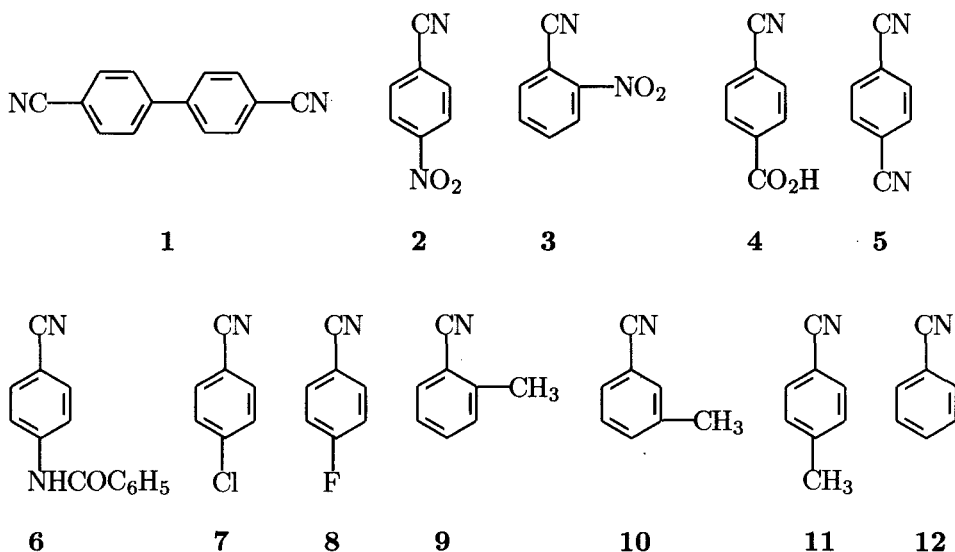
INTRODUCTION

Up to date, the most catalysts used for the polymerization of aromatic and heterocyclic nitriles are Lewis acid^[1-5] or protonic acid^[6-8]. However, these catalysts have some drawbacks, especially the polymerization rate is not high enough to satisfy for the application. In the previous paper^[9], we reported the polymerization kinetics of benzonitrile catalyzed by metal acetylacetonates and found that it is a more preferable catalyst for the polymerization of aromatic nitriles. In this paper, we wish to report the polymerization kinetics of 4,4'-biphenyldicarbonitrile, a typical aromatic dinitrile, and other substituted benzonitriles catalyzed by cobaltic acetylacetonate and also the structure of the polymer obtained.

EXPERIMENTAL

Cobaltic acetylacetonate was prepared according to the literature procedure^[9], and purified by sublimation.

The following twelve nitriles were chosen for research:



Nitriles **1**—**6** were purified by sublimation and **7**—**12** by distillation.

The polymerization was carried out in a sealed glass tube under controlled temperature (250—290°C) with the precision of $\pm 0.5^\circ\text{C}$. The concentration of the unreacted cyano group of nitriles **1**—**6** were measured by infrared spectroscopic method^[2] using potassium ferricyanide as the internal standard and that of **7**—**12** were measured by weighing method^[4]. The determination of polymer structure was carried out by extraction method^[9].

RESULTS AND DISCUSSION

1. Polymerization of 4,4'-biphenyldicarbonitrile catalyzed by cobaltic acetylacetonate

The polymerization of 4,4'-biphenyldicarbonitrile (**1**) catalyzed by cobaltic acetylacetonate was carried out in molar ratio of cyano group to catalyst in 1 to 0.02 at 250, 260, 270, 280 and 290°C, respectively. It has been indicated that the polymerization kinetics of benzonitrile catalyzed by metal acetylacetonates can be expressed as^[9]:

$$V_{\text{polym}} - d[\text{CN}]/dt = k'[\text{CN}]^2 = k[\text{Cat}][\text{CN}]^2$$

$$\text{or } [\text{CN}]^{-1} - [\text{CN}]_0^{-1} = k't = kt[\text{Cat}]$$

The plot of $[\text{CN}]^{-1} - [\text{CN}]_0^{-1}$ against polymerization time at different temperatures is shown in Fig.1. A series of straight lines passing through the origin of coordinates denotes that the above kinetics expression is also suitable for the polymerization of **1**. The rate constants of polymerization calculated from the slopes of the straight lines in Fig.1 are: 0.0539, 0.0886, 0.1347, 0.2096 and 0.3287 $\text{mol}^{-2}\text{L}^2\text{h}^{-1}$ at 250, 260,

270, 280 and 290°C, respectively. The activation energy obtained from Arrhenius plot is 112.78KJ/mol and frequency factor is $9.644 \times 10^9 \text{L}^2 \text{mol}^{-2} \text{h}^{-1}$.

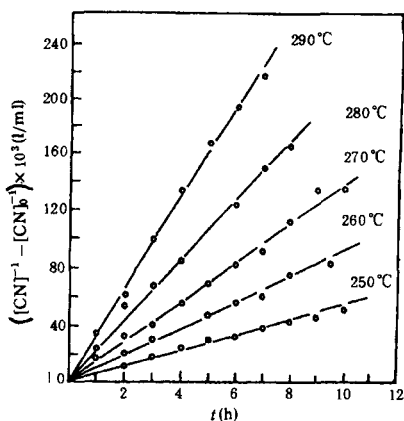


Fig. 1 The relation between $[\text{CN}]^{-1} - [\text{CN}]_0^{-1}$ and time of polymerization of 4,4'-biphenyl-dicarbonitrile catalyzed by cobaltic (III) acetylacetonate
 $[\text{CN}]_0 / [\text{Co}(\text{acac})_3] = 1/0.02$

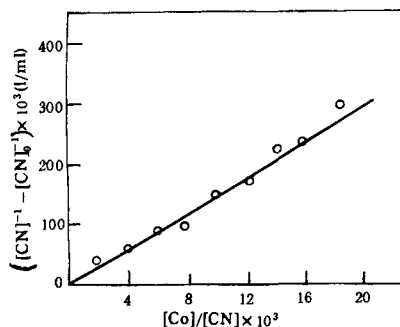


Fig.2 The relation between $[\text{CN}]^{-1} - [\text{CN}]_0^{-1}$ and $[\text{Co}]/[\text{CN}]_0$ of 4,4'-biphenyldi-carbonitrile polymerization
 Catalyst: $\text{Co}(\text{acac})_3$ polymn.
 temp.: 270°C, polymn. time: 10h.

The polymerization of **1** catalyzed by different concentration of cobaltic acetylacetonate was also studied. The relation between $[\text{CN}]^{-1} - [\text{CN}]_0^{-1}$ and $[\text{Cat}]/[\text{CN}]_0$ shown in Fig.2 indicates also a straight line passing through the origin. The rate constant obtained from this figure is $0.1614 \text{mol}^{-2} \text{L}^2 \text{h}^{-1}$ at 270°C, and is nearly the same as from Fig.1. This proves further the above kinetics equation being correct for the polymerization of **1**.

Table 1 Polymerization rate constants of different substituted benzonitriles

Benzonitriles	2	3	4	5	6	7
$k(\text{mol}^{-2} \text{L}^2 \text{h}^{-1})$	0.1394	0.3035	0.1004	0.2013	0.1171	0.0248
Benzonitriles	8	9	10	11	12	
$k(\text{mol}^{-2} \text{L}^2 \text{h}^{-1})$	0.0292	0.00787	0.0407	0.0229	0.0589 ^[9]	

Polymerization temperature: 270°C

$[\text{CN}]_0 / [\text{Co}(\text{acac})_3] = 1/0.02$

2. Polymerization of different substituted benzonitriles

The polymerization of different substituted benzonitriles **2—11** catalyzed by cobaltic acetylacetonate were carried out at 270°C, and benzonitrile (**12**) was used

as reference. The plots of $[\text{CN}]^{-1} - [\text{CN}]_0^{-1}$ against time shown in Fig.3—5 indicate also a series of straight lines passing through origin. The rate constants calculated from these figures are listed in Table 1. From the data of this Table, it can be seen obviously that the polymerization rate is greatly affected by the electronic effect of the substituent. We have reported the results of polymerization of some different

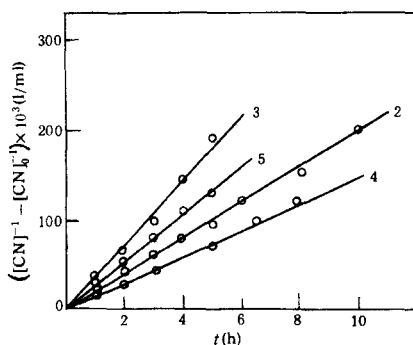


Fig.3 The relation between $[\text{CN}]^{-1} - [\text{CN}]_0^{-1}$ and time of polymerization of **2—5** catalyzed by cobaltic (III) acetylacetonate

$[\text{CN}]_0/[\text{Co}(\text{acac})_3] = 1/0.02$ polymn. temp.: 270°C

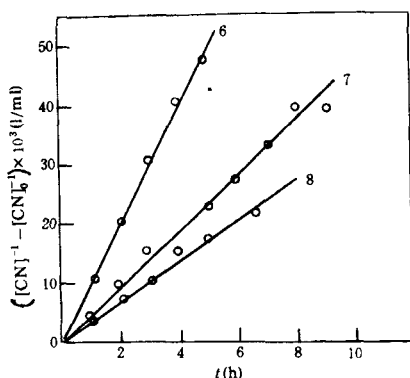


Fig. 4 The relation between $[\text{CN}]^{-1} - [\text{CN}]_0^{-1}$ and time of polymerization of **6—8** catalyzed by cobaltic (III) acetylacetonate

$[\text{CN}]_0/[\text{Co}(\text{acac})_3] = 1/0.02$

polymn. temp. = 270°C

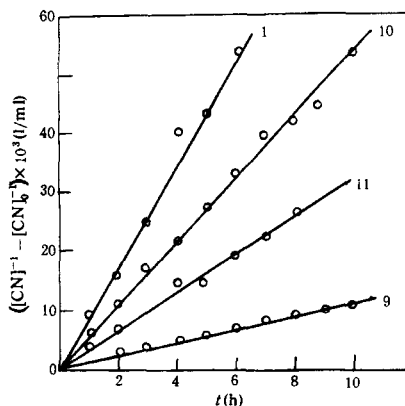


Fig.5 The relation between $[\text{CN}]^{-1} - [\text{CN}]_0^{-1}$ and time of polymerization of **1 and 9—11** catalyzed by cobaltic(III) acetylacetonate

$[\text{CN}]_0/[\text{Co}(\text{acac})_3] = 1/0.02$

polymn. temp.: 270°C

substituted benzonitriles catalyzed by cuprous chloride-zinc system^[10]. In comparison with these two results, the general tendency is consistent, i.e. the electron withdrawing substituent favors the polymerization of benzonitriles and that is also coincident to the mechanism proposed by us^[9]. However, the details of these two

results show some differences especially the conjugation effect of substituent is more preferable in the case of cobaltic acetylacetonate using as catalyst, such as for **7** and **8**.

Table 2 The ratio of linear to cyclic structure of polymers of different substituted benzonitriles

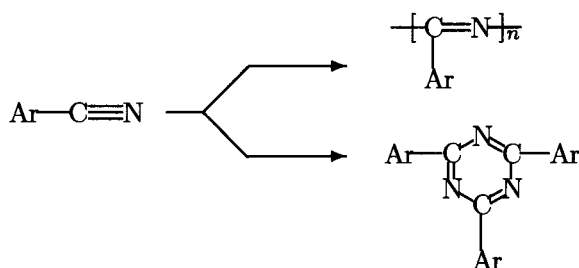
Ar—CN	Conversion	Ratio linear/cyclic
	%	
C ₆ H ₅ —CN	79	0/100
<i>p</i> -CH ₃ C ₆ H ₄ —CN	—	0/100
<i>m</i> -CH ₃ C ₆ H ₄ —CN	54	15/85
<i>p</i> -FC ₆ H ₄ —CN	95	67/33
<i>p</i> -ClC ₆ H ₄ —CN	70	21/79
<i>p</i> -BrC ₆ H ₄ CN	—	58/42
<i>p</i> -(C ₆ H ₅ CONH)C ₆ H ₄ CN	—	40/60
<i>p</i> -[C ₆ H ₄ (CO) ₂ N]—C ₆ H ₄ —CN	—	92/8
<i>p</i> -NO ₂ C ₆ H ₄ —CN	100	100/0
<i>o</i> -NO ₂ C ₆ H ₄ —CN	—	79/21
<i>p</i> -CNC ₆ H ₄ —CN	100	100/0

Polymerization temperature: 300°C Polymerization time: 100 h.

[CN]₀/[Co(acac)₃] = 1/0.05

3. Polymer structure from different benzonitriles

Two types of polymer structure may be formed from the polymerization of benzonitriles according to:



The one is a linear polymer with carbon nitrogen double bond backbone, and another is triaryl-s-triazine structure by cyclotrimerization^[4]. The ratios of linear to cyclic structure of polymers of different substituted benzonitriles catalyzed by cobaltic acetylacetonate are listed in Table 2. From this table, it is indicated that the more linear structure of the polymer is formed from the benzonitriles with the

more electron withdrawing substituents. In comparison with the results catalyzed by cuprous chloride-zinc system^[10], more linear structure polymer is formed from the benzonitriles catalyzed by cobaltic acetylacetonate.

Keywords:

Substituted benzonitrile; Polymerization; Cobaltic acetylacetonate

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