

# AROMATIC AND HETEROCYCLIC NITRILES AND THEIR POLYMERS XVI. THE POLYMERIZATION KINETICS OF 4, 4'-BIPHENYLDICARBONITRILE CATALYZED BY LEWIS ACID-METAL SYSTEM

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## ABSTRACT

The polymerization kinetics of 4,4'-biphenyldicarbonitrile using cuprous chloride-zinc system as catalyst was investigated. the concentration of unreacted cyano group was measured by infrared spectroscopic analysis using potassium ferricyanide as the internal reference. It was found that the polymerization rate is directly proportional to the concentrations of cyano group, cuprous chloride and zinc, and the activation energy of the polymerization is as low as 18.4 KJ/mol. In addition, the other kinetics parameters were obtained and discussed.

The polymerization of aromatic and heterocyclic dinitriles using Lewis acid as catalyst has been thoroughly studied in our laboratory<sup>[1-3]</sup>. The polymer obtained contains aromatic and s-triazine ring in the main chain and possesses excellent oxidative thermal stability.

Taking Lewis acid as catalyst, the polymerization rate is not high enough to satisfy the needs of the technology of capped polyimide for the preparation of composite materials. In the previous paper, we reported the results of investigation on the catalyst for the polymerization of aromatic nitriles. It was found that Lewis acid-metal is a preferable catalyst system and the polymerization rate is about 10 times faster than Lewis acid alone<sup>[4]</sup>.

The results of polymerization kinetics and mechanism of 4,4'-biphenyldicarbonitrile catalyzed by zinc chloride have been published<sup>[3]</sup>. In this paper, the polymerization kinetics of 4,4'-biphenyldicarbonitrile catalyzed by Lewis acid-metal system is presented.

## EXPERIMENTAL

The polymerization was carried out in sealed glass tube under given temperature in the range of 240 — 290 °C with the accuracy of  $\pm 0.1$  °C. The concentration of unreacted cyano group was measured by infrared spectroscopic analysis using potassium ferricyanide as internal reference, and calculated by means of the working curve plotted by the ratio of absorbance versus the molar ratio of monomer to internal reference<sup>[2]</sup>.

## RESULTS AND DISCUSSION

### 1. Polymerization kinetics of 4,4'-biphenyldicarbonitrile catalyzed by cuprous chloride

The polymerization of 4,4'-biphenyldicarbonitrile catalyzed by zinc chloride has been studied. It was found that the polymerization rate is directly proportional to concentrations of cyano group and Lewis acid<sup>[2,3]</sup>. While zinc chloride is hygroscopic, it makes some troubles for the experiment. In this paper, we chose the cuprous chloride as catalyst for the polymerization of 4,4'-biphenyl-dicarbonitrile to avoid the above trouble. The molar ratio of monomer to catalyst is 1 to 0.025. The conversion of cyano group was measured at 240, 250, 260, 270, 280 and 290 °C, respectively. The plot of  $-\ln[\text{CN}]/[\text{CN}]_0$  against polymerization time is shown in Fig. 1. It indicates that the polymerization rate is directly proportional to the concentration of cyano group.

The polymerization of 4,4'-biphenyldicarbonitrile was also carried out by using different concentration of cuprous chloride. The plot of  $-\ln[\text{CN}]/[\text{CN}]_0$  against concentration of cuprous chloride is shown in Fig. 2. The results show that the polymerization rate is also directly proportional to the concentration of cuprous chloride. Therefore, the polymerization kinetics of 4,4'-biphenyldicarbonitrile catalyzed

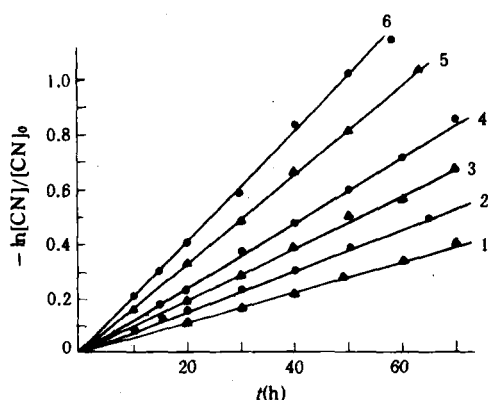


Fig. 1 The polymerization of 4,4'-biphenyldicarbonitrile catalyzed by cuprous chloride  
monomer/ $\text{Cu}_2\text{Cl}_2$  = 1/0.025 molar ratio;  
Temp.: 1-240; 2-250; 3-260; 4-270;  
5-280; 6-290 °C.

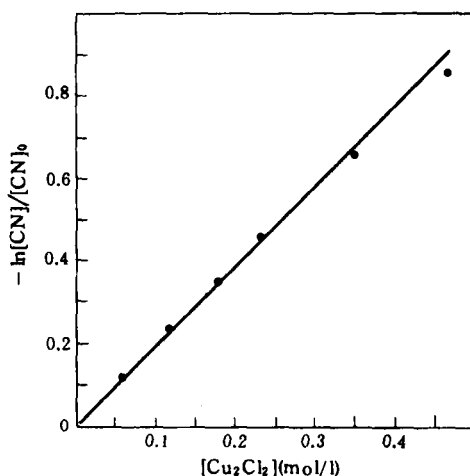


Fig. 2 The relation between  $-\ln[\text{CN}]/[\text{CN}]_0$  and concentration of cuprous chloride for the polymerization of 4,4'-biphenyldicarbonitrile  
Temp.: 270 °C; time: 20 h.

Table 1 The rate constants and activation energy of polymerization of 4,4'-biphenyldicarbonitrile catalyzed by different catalysts

| $k \times 10^4$<br>Catalyst          | 240    | 250    | 260   | 270   | 280   | 290   | $E_a$<br>(KJ/mol)   |
|--------------------------------------|--------|--------|-------|-------|-------|-------|---------------------|
| $\text{Cu}_2\text{Cl}_2$             | 0.0631 | 0.0875 | 0.112 | 0.141 | 0.198 | 0.251 | 64.5                |
| $\text{Cu}_2\text{Cl}_2 - \text{Zn}$ | 1.62   | 1.74   | 1.86  | 1.98  | 2.17  | 2.34  | 18.4                |
| $\text{ZnCl}_2$                      |        |        | 1.072 | 1.417 | 1.736 | 2.189 | 58.2 <sup>[3]</sup> |

\*  $k$  ( $\text{l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ )

by cuprous chloride, like zinc chloride, can be expressed as the following equation :

$$V_{\text{polym.}} = - \frac{d[\text{CN}]}{dt} = k' \cdot [\text{CN}]^k \cdot [\text{Cu}_2\text{Cl}_2] \cdot [\text{CN}] \quad (1)$$

From the results shown in Fig. 1, the rate constants of polymerization calculated based on the above equation are listed in Table 1. The activation energy obtained from Arrhenius plot is 64.5 KJ/mol showing in Table 1.

## 2. Polymerization kinetics of 4,4'-biphenyldicarbonitrile catalyzed by Lewis acid-metal system

In our previous paper <sup>[4]</sup>, it was found that Lewis acid-metal system, such as zinc chloride-zinc, cuprous chloride-zinc, aluminium chloride-zinc or cobaltous chloride-zinc can be used as catalyst for the polymerization of aromatic nitriles, and the polymerization is much faster than using Lewis acid alone. It was also found that the polymerization rate is proportional to the concentration of cyano group.

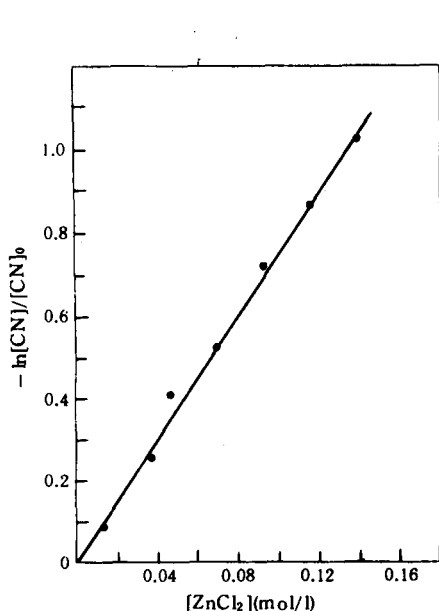


Fig. 3 The relation between  $-\ln[\text{CN}]/[\text{CN}]_0$  and the concentration of zinc chloride for the polymerization of 4,4'-biphenyldicarbonitrile catalyzed by zinc chloride - zinc system  
Temp. = 270 °C ; time : 10 h ;  
monomer/Zn = 1/0.025 molar ratio.

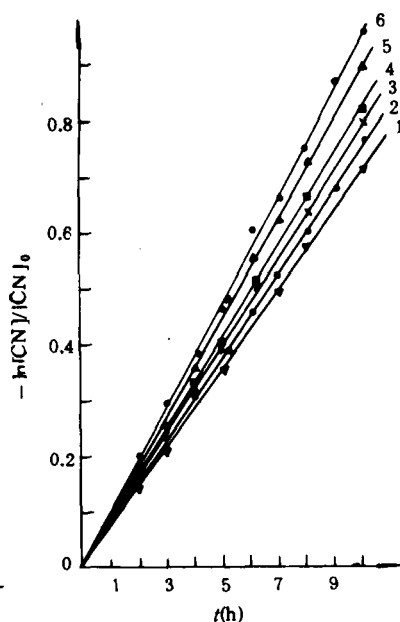


Fig. 4 The relation between  $-\ln[\text{CN}]/[\text{CN}]_0$  and time for the polymerization of 4,4'-biphenyldicarbonitrile catalyzed by cuprous chloride-zinc system  
monomer/ $\text{Cu}_2\text{Cl}_2$ /Zn = 1/0.025/0.05 molar ratio ;  
Temp.: 1 - 240; 2 - 250; 3 - 260; 4 - 270; 5 - 280; 6 - 290 °C .

The reaction was carried out using zinc chloride-zinc catalyst system with different concentration of zinc chloride at a given temperature ( 270 °C ) and time (10h), and the conversion of 4,4'-biphenyldicarbonitrile was determined. Plot of  $-\ln[\text{CN}]/[\text{CN}]_0$  to the concentration of zinc chloride is shown in Fig. 3, a straight line passing through the origin of coordinates was obtained. It shows that the polymerization rate is also directly proportional to the concentration of zinc chloride.

Hence, we come to conclusion that the polymerization rate of 4,4'-biphenyldicarbonitrile catalyzed by zinc chloride-zinc system is directly proportional to the concentrations of cyano group and zinc chloride, and the kinetics can be expressed as follows:

$$V_{\text{polym.}} = - \frac{d[\text{CN}]}{dt} = k' \cdot [\text{CN}] = k \cdot [\text{ZnCl}_2] \cdot [\text{CN}] \quad (2)$$

As mentioned above, zinc chloride is hygroscopic, and it makes some troubles for the experiment. Therefore, we chose cuprous chloride-zinc system as catalyst for the further investigation.

Fig. 4 shows the results of the polymerization of 4,4'-biphenyldicarbonitrile catalyzed by cuprous chloride-zinc catalyst system in the molar ratio of monomer/ $\text{Cu}_2\text{Cl}_2/\text{Zn} = 1/0.025/0.05$ . The polymerization rate constants are also listed in Table 1. In this catalyst system, the actual catalyst is zinc chloride-zinc due to the redox reaction between cuprous chloride and zinc. This fact has been proved by the constitution analysis of the catalyst system and also confirmed by the nearly identical experiment results obtained by use of zinc chloride-zinc system in molar ratio of monomer/ $\text{ZnCl}_2/\text{Zn} = 1/0.025/0.025$ .

The polymerization of 4,4'-biphenyldicarbonitrile catalyzed by cuprous chloride-zinc system with different amount of zinc was also measured. The results are shown in Fig. 5 and Fig. 6. It indicates that the polymerization rate is directly proportional to the concentration of zinc, too. Only in the case of large amount of zinc used, the point is deviated from the straight line as showing in Fig. 6. Therefore, the

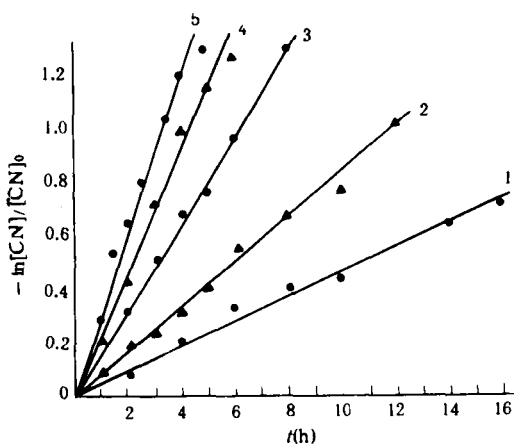


Fig. 5 The polymerization of 4,4'-biphenyldicarbonitrile catalyzed by cuprous chloride-zinc system  
Temp.: 270 °C  
monomer/ $\text{Cu}_2\text{Cl}_2 = 1/0.025$  molar ratio;  
monomer/Zn = 1/0.025 (1); 1/0.05 (2); 1/0.10 (3);  
1/0.15 (4); 1/0.20 (5).

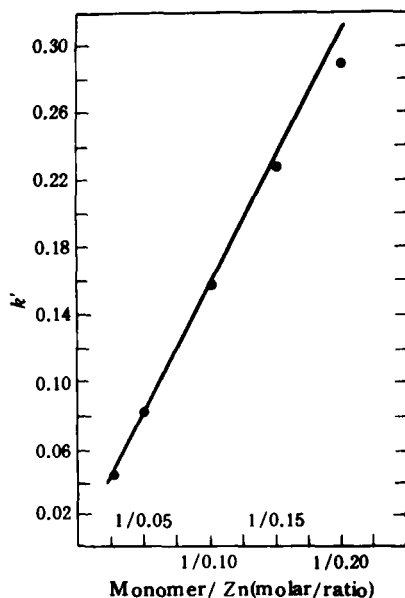


Fig. 6 The relation between  $k'$  and the concentration of zinc for the polymerization of 4,4'-biphenyldicarbonitrile catalyzed by cuprous chloride-zinc system  
Temp.: 270 °C;  
monomer/ $\text{Cu}_2\text{Cl}_2 = 1/0.025$  molar ratio.

polymerization kinetics of 4,4'-biphenyldicarbonitrile catalyzed by cuprous chloride-zinc system can be expressed as the following equation:

$$V_{\text{polym.}} = -\frac{d[\text{CN}]}{dt} = k' \cdot [\text{CN}] = k \cdot [\text{Cu}_2\text{Cl}_2] \cdot [\text{CN}] = k'' \cdot [\text{Zn}] \cdot [\text{Cu}_2\text{Cl}_2] \cdot [\text{CN}] \quad (3)$$

### 3. The other kinetics parameters

The activation energy and frequency factor for the polymerization of 4,4'-biphenyldicarbonitrile can be obtained from the Arrhenius equation and are listed in Table 2. As mentioned previously<sup>[6]</sup>, the low activation energy and very low frequency factor due to the rigid molecule of aromatic dinitrile are the characteristics of the polymerization of aromatic nitrile. From the data in Table 2, we can see that the activation energy for the polymerization of 4,4'-biphenyldicarbonitrile catalyzed by cuprous chloride-zinc system is as low as 18.4 KJ/mol and much lower than catalyzed by Lewis acid alone. The frequency factor is so lower that the value is rather unreasonable. This problem can be rationalized by modification of Arrhenius equation (Eq. 4) by the addition of a steric factor  $P$  showing as Eq. 5<sup>[7]</sup>.

$$k = A \cdot \exp(-E_a / RT) \quad (4)$$

$$k = P \cdot A' \cdot \exp(-E_a / RT) \quad (5)$$

The factor  $P$  represents the fraction of energetically suitable collisions for which the orientation is also favorable, and it can be calculated by the activated complex theory<sup>[8]</sup>. The data calculated are also listed in Table 2. The value of  $A'$  obtained from the theory is about  $1 \times 10^{13} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , while the  $P$  is much lower. The low value of  $P$  denotes the more special steric requirement for reaction. Therefore, the

**Table 2** Kinetics parameters for the polymerization of 4,4'-biphenyldicarbonitrile catalyzed by different catalysts

| Catalyst                           | $E_a$<br>(KJ/mol)   | $A$<br>( $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ) | $P$                   |
|------------------------------------|---------------------|-----------------------------------------------------------------|-----------------------|
| $\text{Cu}_2\text{Cl}_2$           | 64.5                | 23.7                                                            | $1.8 \times 10^{-12}$ |
| $\text{ZnCl}_2$                    | 58.2 <sup>[3]</sup> | 58 <sup>[6]</sup>                                               | $4.5 \times 10^{-12}$ |
| $\text{Cu}_2\text{Cl}_2\text{-Zn}$ | 18.4                | 0.012                                                           | $1.0 \times 10^{-15}$ |

very low value of steric factor for the polymerization of 4,4'-biphenyldicarbonitrile catalyzed by cuprous chloride zinc system indicates that this polymerization requires more special orientation for the energetically suitable collisions.

### Keywords:

Aromatic Nitrile; polymerization; Kinetics

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