

THE AROMATIC AND HETEROCYCLIC DINITRILES AND THEIR POLYMERS. IX. THE POLYMERIZATION KINETICS OF 4,4'-BIPHENYLDICARBONITRILE*

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ABSTRACT

The polymerization kinetics of 4,4'-biphenyldicarbonitrile catalyzed by complex of 4,4'-biphenyldicarbonitrile with ZnCl_2 was studied. The cyano group concentration was measured by infrared spectroscopic analysis using potassium ferricyanide as the internal reference. The results proved that the polymerization is a second order reaction, and the activation energy of polymerization is 12.4 kcal/mol. The polymerization rates of 4,4'-biphenyldicarbonitrile catalyzed by other seven complexes were also measured. The polymerization mechanism was discussed.

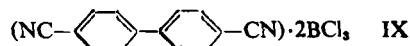
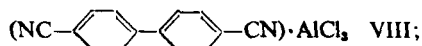
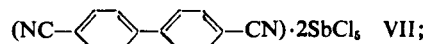
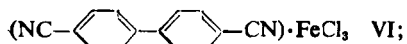
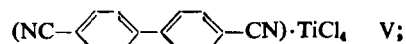
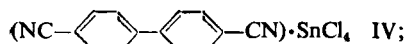
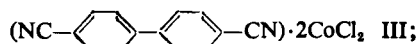
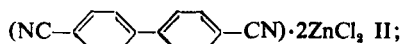
Aromatic dinitriles can be polymerized to a crosslinked polymer containing aromatic and s-triazine ring in the main chain in the presence of chlorosulfonic acid^[1] or Lewis acid^[2]. It is difficult to study the polymerization kinetics and mechanism and constitution of polymers, because these polymer are insoluble and infusible. Marvel et al.^[3] have reported the syntheses of crosslinked polymer by cyclopolymerization of the low molecular weight aromatic ether, ketone and sulfone containing pendant cyano group and the measurement of the concentration of the unreacted cyano group by infrared spectroscopic analysis based on relative intensity method, but the error was rather large. In present report we measured more accurately the content of the unreacted cyano group in the crosslinked polymer by infrared spectroscopy using potassium ferricyanide as the internal reference in paraffin paste. By means of this quantitative analysis we studied the polymerization kinetics of 4,4'-biphenyldicarbonitrile (I) catalyzed by complex of 4,4'-biphenyldicarbonitrile with ZnCl_2 and the influence of complexes of 4,4'-biphenyldicarbonitrile with other chlorides on polymerization rate and the polymerization mechanism of 4,4'-biphenyldicarbonitrile catalyzed by Lewis acid was discussed.

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EXPERIMENTAL

4,4'-biphenyldicarbonitrile was prepared by Sandmeyer reaction of 4,4'-diaminobiphenyl with KCN catalyzed by NiCl_2 , and purified by sublimation. m. p. 232—234°C.

The complexes II—IX of 4,4'-biphenyldicarbonitrile with ZnCl_2 and other chlorides were prepared by 4,4'-biphenyldicarbonitrile with the appropriated chlorides^[4]:



Their melting points were listed in Table 1.

In order to remove moisture from the system, 4,4'-biphenyldicarbonitrile and its complex with chloride (molar ratio 1:0.02) were mixed and put into glass tube, then placed in a desiccator containing P_2O_5 for a week. The glass tube was sealed under evacuation and heated under controlled temperature (260—300°C), then the concentration of unreacted cyano group was measured at appointed intervals. The volume effect was corrected.

The concentration of unreacted cyano group was measured by infrared spectroscopic analysis using potassium ferricyanide as the internal reference in paraffin paste. Absorption peaks of cyano group of potassium ferricyanide and polymer were recorded by SHIMADZU IR-430 spectrophotometer. The absorbance was obtained from transmittance. The concentration of cyano group was calculated by means of the "working curve" which was plotted by the ratio of absorbance ($A_{\text{CN}}/A_{\text{K}}$) versus the molar ratio of 4,4'-biphenyldicarbonitrile (M_{CN}) and ferricyanide (M_{K}) as in Fig. 1.

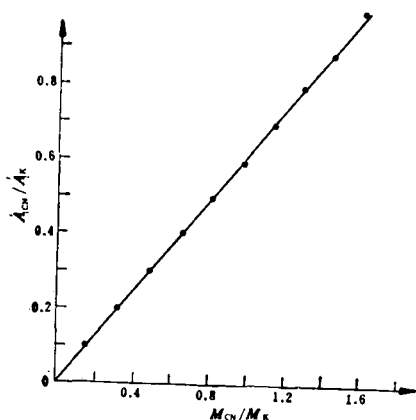


Fig. 1 Working curve

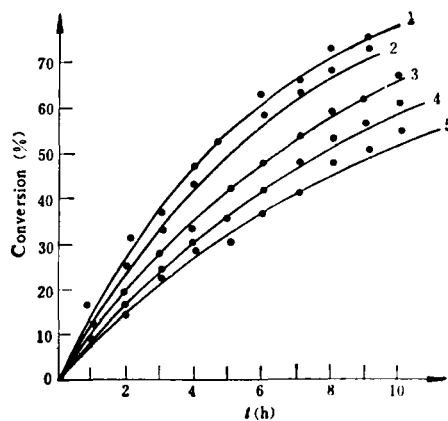


Fig. 2 The plot of conversion of cyano group versus time
1 300°; 2 290°; 3 280°; 4 270°; 5 260°.

RESULTS AND DISCUSSION

Polymerization kinetics of 4,4'-biphenyldicarbonitrile catalyzed by complex of 4,4'-biphenyldicarbonitrile with ZnCl_2

The conversion of 4,4'-biphenyldicarbonitrile (molar ratio of monomer to catalyst: $\text{NC}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN} : (\text{NC}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}) \cdot 2\text{ZnCl}_2 = 1:0.02$) was determined at 260, 270, 280, 290, 300°C respectively. The results are shown in Fig. 2.

The plot of $\ln[\text{CN}]_0/[\text{CN}]$ with time is shown in Fig. 3. It shows that the polymerization rate is directly proportional to the concentration of cyano group.

The rates of polymerization catalyzed by complex of different concentrations are shown in Fig. 4.

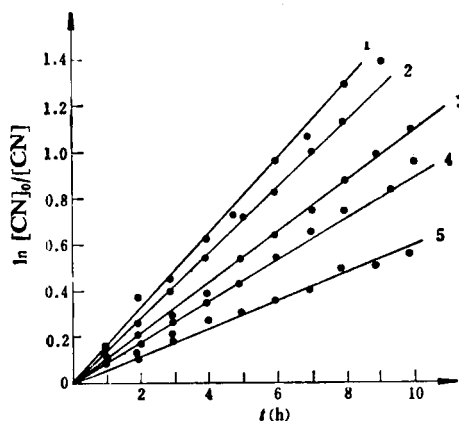


Fig. 3 The relation between $\ln[\text{CN}]_0/[\text{CN}]$ and time
1 300°; 2 290°; 3 280°; 4 270°; 5 260°.

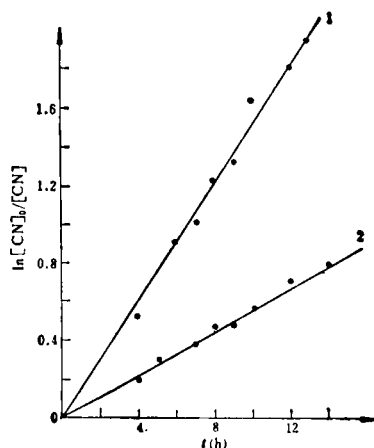


Fig. 4 The rates of polymerization of cyano group catalyzed by complex of different concentration Temp.: 260°C
1 $0.2256 \text{ mol} \cdot \text{L}^{-1}$; 2 $0.08908 \text{ mol} \cdot \text{L}^{-1}$.

The results indicate that the rate of polymerization increases remarkably with the increase of concentration of complex. Although the concentration of complex has a great influence upon the rate of polymerization, the peak altitude of cyano group of complex (2275 cm^{-1}) neighbouring but separating distinctly from the peak of cyano group of 4,4'-biphenyldicarbonitrile (2228 cm^{-1}) keep constant during the reaction. It means that the concentration of cyano group of complex keep constant during the polymerization. This denotes that the complex of 4,4'-biphenyldicarbonitrile with ZnCl_2 only plays a role of catalyst in the polymerization of 4,4'-biphenyldicarbonitrile. In addition, the conversion of 4,4'-biphenyldicarbonitrile catalyzed by complex of different concentration at the given temperature (290°C) and time (5hr) were measured. The plot of $\ln[\text{CN}]_0/[\text{CN}]$ against concentration of complex is shown in Fig. 5. It shows that the polymerization rate is also directly proportional to the concentration of complex.

Therefore, the polymerization kinetics of 4,4'-biphenyldicarbonitrile catalyzed by complex of 4,4'-biphenyldicarbonitrile with ZnCl_2 can be expressed as follows:

$$V_{\text{poly}} = -\frac{d[\text{CN}]}{dt} = k \cdot [\text{complex}] [\text{CN}] = k' [\text{CN}] \quad (1)$$

where $k' = k \cdot [\text{complex}]$. This equation is also proved by the constant k value obtained from dividing the k' by respective concentration of complex.

The rate constants of polymerization calculated by above mentioned equation are: 0.40; 0.53; 0.62; 0.82; 0.90 $\text{L} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ at 260; 270; 280; 290; 300°C, respectively. The activation energy obtained from Arrhenius plot (Fig. 6) is 12.4 kcal/mol and the frequency factor is $6.2 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$. The activation energy of this polymerization is very low, therefore the reason of the rather drastic polymerization condition is due to the lower frequency factor. Since 4,4'-biphenyldicarbonitrile is a rigid molecule, so that the effective collision is relative low.

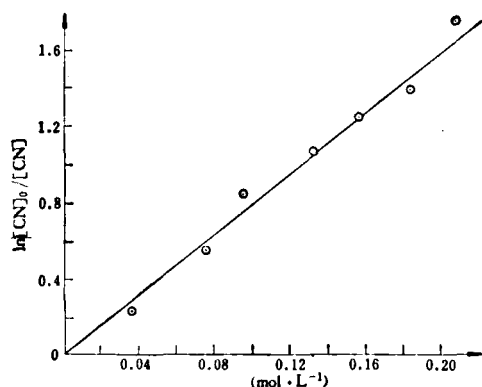


Fig. 5 The relation between the concentration of catalyst and $\ln[\text{CN}]_0/[\text{CN}]$
 t : 5hr; Temp.: 290°C.

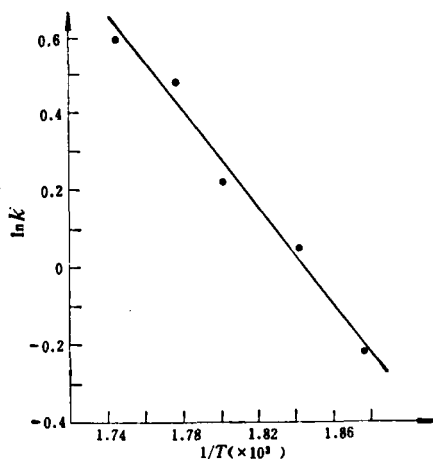


Fig. 6 The relation between $\ln k$ and $1/T$

Influence of different complexes of 4,4'-biphenyldicarbonitrile with chloride on the polymerization rate of 4,4'-biphenyldicarbonitrile

We take eight complexes of 4,4'-biphenyldicarbonitrile with chloride as catalysts for polymerization of 4,4'-biphenyldicarbonitrile respectively, the results are shown in Fig. 7. Their rate constants of polymerization at 280°C are: V 0.70; II 0.62; VI 0.44; III 0.33; IV 0.22; VIII 0.20; VII 0.098; IX 0.023 ($\text{L} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$). It indicates that the catalytic ability of various complexes of 4,4'-biphenyldicarbonitrile with chloride for polymerization of 4,4'-biphenyldicarbonitrile is quite different. Among them the complexes with TiCl_4 and ZnCl_2 are better catalyst, and the complex with BCl_3 is the weakest catalyst. The reason why these complexes have such different catalytic activity is the different coordination ability of lone pair electron on the nitrogen atom of the cyano group with empty orbit of metal. We have measured the binding energy of nitrogen atom of these eight 4,4'-biphenyldicarbonitrile.

chloride complexes by X-ray photoelectron spectroscopy (XPS)^[5]. The results are listed in Table 1. From Table 1 it is obvious that the N_{1s} binding energy of these complexes is higher than that of 4,4'-biphenyldicarbonitrile. In general, the higher N_{1s} binding energy shift the complex possesses, the better is the catalyst. The N_{1s} binding energy shift of complex of 4,4'-biphenyldicarbonitrile with BCl_3 is the lowest, therefore its catalytic activity is the weakest.

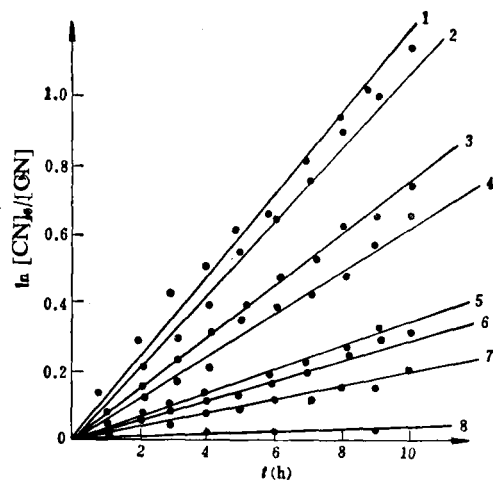


Fig. 7 The polymerization of 4,4'-biphenyldicarbonitrile catalyzed by eight complexes of 4,4'-biphenyldicarbonitrile with chloride

Temp.: 280°C; amount of catalyst: 1: 0.02 molar ratio (complex: II, III, VII, IX) or 1:0.04 molar ratio (complex: IV, V, VI, VIII)

1 V; 2 II; 3 VI; 4 III; 5 IV; 6 VIII; 7 VII; 8 IX.

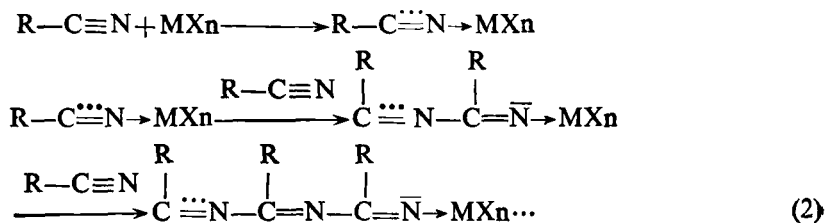
Polymerization mechanism of aromatic dinitrile catalyzed by Lewis acid

According to the experimental results obtained, the following polymerization mechanism of aromatic dinitrile catalyzed by Lewis acid was proposed. At first aromatic dinitrile co-ordinate with Lewis acid to form the molecular complex^[4]. Because the lone pair electron on

Table 1 Melting points and XPS results of complexes of 4,4'-biphenyldicarbonitrile with chloride

Sample	m. p. (°C)	N_{1s} (eV)	ΔN_{1s} (eV)	Sample	m. p. (°C)	N_{1s} (eV)	ΔN_{1s} (eV)
II	302—304	400.1	1.6	VI	252—254	399.6	1.1
III	>340	400.0	1.5	VII	178—180	399.5	1.0
IV	136—138	399.8	1.3	VIII	309—311	399.2	0.7
V	238—240	399.7	1.2	IX	227—231	399.0	0.5
I	232—234	398.5					

the nitrogen atom of the cyano group coordinate with empty orbit of metallic ion, it makes less electron charge on this nitrogen as comparing with that before coordination^[5]. This induces the carbon atom of the cyano group of complex to be more positive, therefore it is favourable for the attack of this cyano group by other 4,4'-biphenyldicarbonitrile molecules. The electron charge density of carbon atom of cyano group in these intermediates is still lower, so it makes polymerization going on. The mechanism can be formulated as follows:



If the rate constants of every cyano addition step are equal, the polymerization rate can be denoted as the following equation:

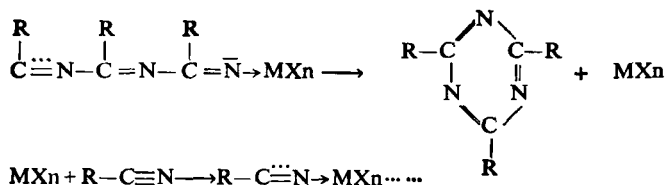
$$-d[\text{CN}]/dt = k[\text{CN}] \left\{ [\text{R}-\text{C}\equiv\text{N} \rightarrow \text{MX}_n] + \sum_{n=0}^{\infty} \left[\begin{array}{c} \text{R} \quad \text{R} \quad \text{R} \\ | \quad | \quad | \\ \text{C}\equiv\text{N} \rightarrow \text{C}=\text{N} \end{array} \right]_m \right\} \quad (3)$$

Because the concentration of complex keeps constant during polymerization, therefore the equation (3) can be simplified to:

$$-\frac{d[\text{CN}]}{dt} = k [\text{complex}] [\text{CN}] \quad (4)$$

This is identical with the kinetics result.

The polymer of 4,4'-biphenyldicarbonitrile catalyzed by Lewis acid is insoluble and infusible, however, 1,3,5-s-triazine ring has been ascertained in the main chain by infrared spectroscopy^[2]. In addition, when benzonitrile reacted at the same condition the product was solely 2,4,6-triphenyl-s-triazine. It is obvious that 4,4'-biphenyldicarbonitrile polymerized to a crosslinked polymer containing s-triazine ring through the cyclotrimerization of cyano group. Therefore, as the polymerization favours the cyclization, 1,3,5-triazine structure is formed, but it is also in accordance with the above deduced polymerization rate equation and the formula (2) can be rewritten as follows:



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