

AROMATIC AND HETEROCYCLIC DINITRILES AND THEIR POLYMERS.

XI. STUDY ON THE POLYMERIZATION OF AROMATIC AND HETEROCYCLIC DINITRILES BY INFRARED SPECTROSCOPY*

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ABSTRACT

The polymerization rates of fourteen aromatic and heterocyclic dinitriles were measured by infrared spectroscopy and compared with that of 4,4'-biphenyldicarbonitrile. The rate is greatly enhanced when an electron withdrawing group is substituted at the para position of cyano group in aromatic dinitriles. The polymerization rates of heterocyclic dinitriles were discussed in terms of π -electron density of the heterocyclic rings.

Aromatic and heterocyclic dinitriles can be polymerized in the presence of chlorosulfonic acid^[1] or Lewis acid^[2] to a new kind of crosslinked polymers containing aromatic and heterocyclic ring in main chain. It is difficult to study the polymerization of dinitriles, especially for their polymerization kinetics, because the polymers obtained are insoluble and infusible. The polymerization of aromatic dinitriles had been studied by using the sublimation method^[2], but this method is not so accurate and only for rough comparison. Several years ago, we had synthesized a series of new heterocyclic dinitriles and studied their polymerization by sublimation method too^[3-5]. Recently, we have devised an infrared spectroscopic method for quantitative determination of concentration of cyano group, and it has been used in the study on polymerization kinetics and mechanism of 4,4'-biphenyldicarbonitrile^[6]. This paper reports the results of reinvestigation on polymerization of aromatic and heterocyclic dinitriles by the infrared spectroscopic method.

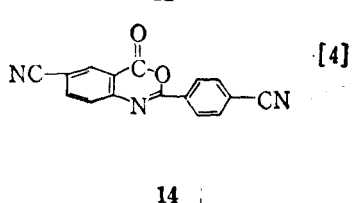
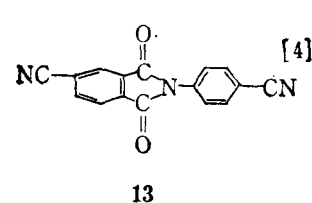
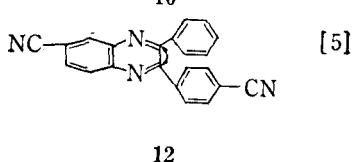
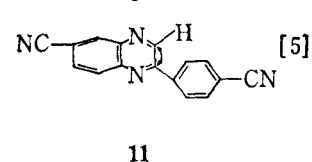
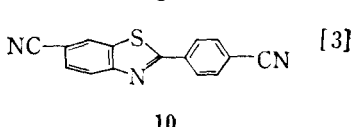
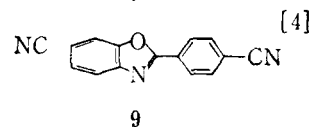
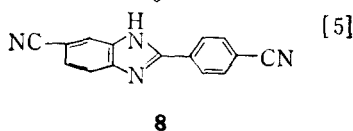
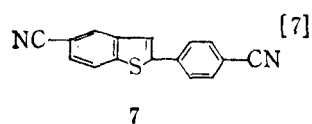
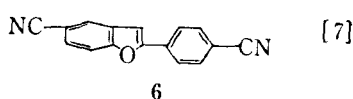
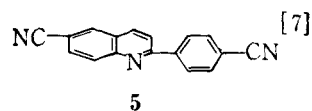
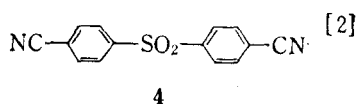
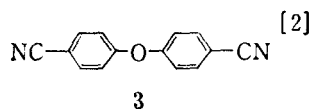
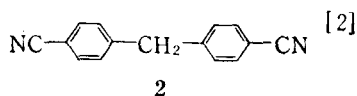
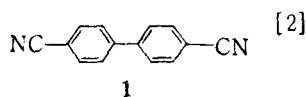
EXPERIMENTAL

The following aromatic and heterocyclic dinitriles were used for investigation, and their preparations were reported elsewhere.

The polymerization was carried out in sealed glass tubes under controlled temperature. The concentration of unreacted cyano group was measured at appointed intervals by infrared spectroscopic analysis using potassium ferricyanide as internal reference according to the procedure reported in literature^[6].

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RESULTS AND DISCUSSION

The polymerization kinetics of 4,4'-biphenyldicarbonitrile (1) catalyzed by complex of 1 with zinc chloride has been studied by us^[6]. The polymerization rate can be expressed as follows:

$$V_{\text{polym.}} = -\frac{d[\text{CN}]}{dt} = k [\text{complex}] [\text{CN}] = k' [\text{CN}]$$

But on study of polymerization of dinitriles with different structures, the preparation of different complex is rather troublesome, therefore we reinvestigate polymerization kinetics of 1 catalyzed directly by zinc chloride. The results are shown in Fig. 1. These results indicate that the polymerization rate of dinitrile is directly proportional to the first order of cyano group concentration, and can be expressed by the above-mentioned equation too. The rate constants shown in Table 1 are nearly the same, irrespective of complex or zinc chloride used as catalyst. Therefore, we can omit the procedure of preparing the different complex of dinitriles with zinc chloride and use zinc chloride directly as catalyst in polymerization rate

measurement. It is convenient for studying polymerization of dinitriles with different structures.

Table 1 Comparison of polymerization rate constants of **1** using complex or ZnCl_2 as catalyst

$k \times 10^4$ ($1 \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$)	Temp. ($^{\circ}\text{C}$)						E_a kcal/mol
	260	270	280	290	300		
Catalyst							
ZnCl_2	1.072	1.417	1.736	2.189			13.9
Complex	1.122	1.467	1.733	2.267	2.511		12.4

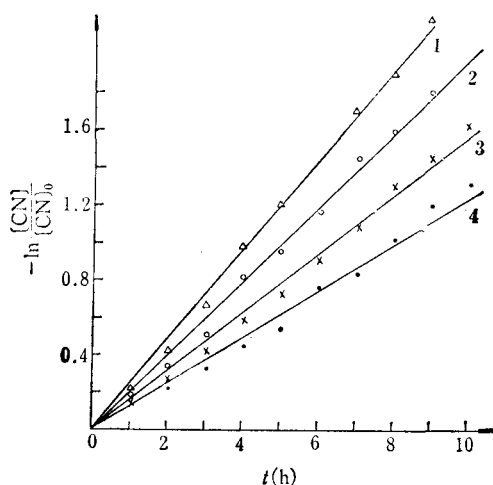


Fig. 1 Correlation between $-\ln \frac{[\text{CN}]}{[\text{CN}]_0}$ and time of polymerization of **1** catalyzed by ZnCl_2 1: ZnCl_2 =1: 0.073 (molar ratio)
1 290; 2 280; 3 270; 4 260 $^{\circ}\text{C}$

Polymerization rate of aromatic dinitriles with different substituents

The polymerization rates of dinitriles **1**–**4** with different substituents using 4 molar percent of zinc chloride as catalyst are measured at 270 $^{\circ}\text{C}$. The results are shown in Fig. 2. It indicates that the polymerization rate is directly proportional to the concentration of cyano group. The rate constants of polymerization of **1**–**4** calculated by the above-mentioned equation are; 1.467; 1.814; 1.444 and $6.444 \times 10^{-4} 1 \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$, respectively. It is obvious that when the substituent in para position is an electron withdrawing group, such as $-\text{SO}_2-$, the polymerization rate of cyano group increases greatly. This can be explained by the mechanism proposed by us^[6]. Thus the polymerization is propagated by the attack of one cyano group on the carbon atom of another cyano group, which is induced to become more positive by complex formation with Lewis acid, and an electron withdrawing group substituted at para position will render this carbon atom more positive, therefore the polymerization is accelerated.

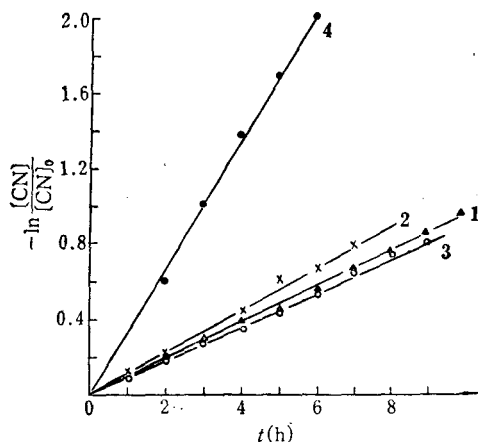


Fig. 2 Correlation between $-\ln \frac{[\text{CN}]}{[\text{CN}]_0}$ and time of polymerization of 1–4 at 270°C

Polymerization rate of heterocyclic dinitriles

The polymerization rates of heterocyclic dinitriles 5–14 with 4 molar percent of zinc chloride as catalyst are determined at 300°C. The results obtained in the following four cases are discussed.

1. Heterocyclic dinitriles with only one hetero-atom in the ring: The results are shown in Fig. 3, and the polymerization rate of 1 under the same conditions is also shown in this figure for comparison. It indicates that the polymerization rate of dinitrile 5 containing quinoline ring is somewhat faster than that of 1, the rate of polymerization of dinitrile 7 containing benzothiophene ring is nearly the same as that of 1, and the rate of polymerization of dinitrile 6 containing benzofuran ring is much slower.

2. Heterocyclic dinitrile with two hetero-atoms in the ring: The results are shown in Fig. 4. In these two dinitriles, the heterocyclic ring contains both one nitrogen atom and

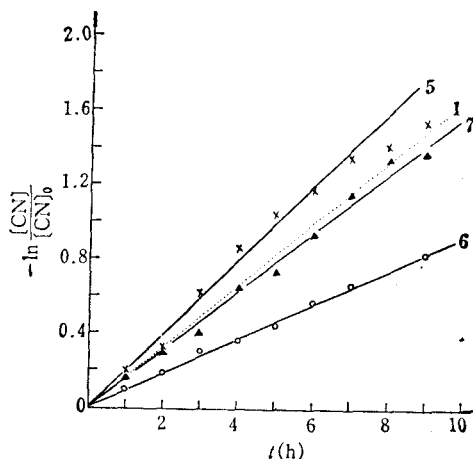


Fig. 3 Correlation between $-\ln \frac{[\text{CN}]}{[\text{CN}]_0}$ and time of polymerization of 5–7

one other hetero-atom, namely oxygen or sulfur. From Fig. 4, it indicates that the polymerization rate of both dinitriles is much faster than that of **1**, but that of dinitrile **10** containing benzothiazole ring is somewhat faster than that of dinitrile **9** containing benzoxazole ring.

3. Heterocyclic dinitriles with two nitrogen atoms in the ring: Since the melting points of dinitrile **8** containing benzimidazole ring and **11** containing quinoxaline ring are higher than 300°C, therefore the polymerization rates of these two dinitriles were determined at 340°C and that of **12** containing also quinoxaline ring with a phenyl substituent both at 300° and 340°C for comparison. The results are shown in Fig. 5. It indicates that the polymerization rates of these three dinitriles are all nearly the same as that of **1**.

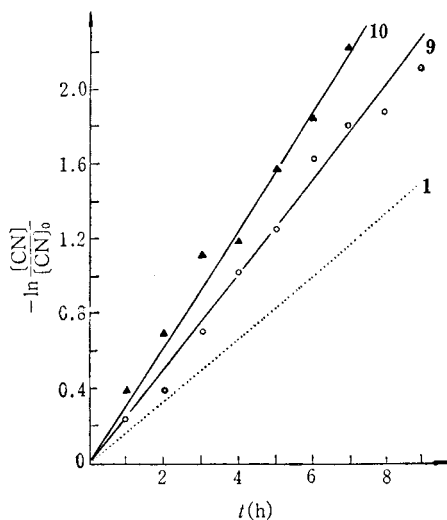


Fig. 4 Correlation between $-\ln \frac{[\text{CN}]}{[\text{CN}]_0}$ and time of polymerization of **9** and **10**

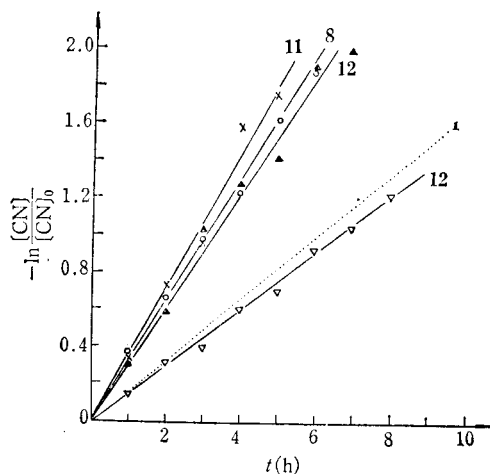


Fig. 5 Correlation between $-\ln \frac{[\text{CN}]}{[\text{CN}]_0}$ and time of polymerization of **8**, **11**, and **12**

4. Heterocyclic dinitriles with $\text{—}\overset{\text{O}}{\parallel}\text{C—N—}$ or $\text{—}\overset{\text{O}}{\parallel}\text{C—O—}$ linkage in the ring: The polymerization rates of all the above aromatic or heterocyclic dinitriles using zinc chloride as catalyst are proportional to the first order of cyano group concentration, i.e. correlation between $-\ln \frac{[\text{CN}]}{[\text{CN}]_0}$ and time are linear. But the correlation between $-\ln \frac{[\text{CN}]}{[\text{CN}]_0}$ and polymerization time of dinitrile **13** containing phthalimide ring and **14** containing benzoxazinone ring are not linear, the curve bends downwards as shown in Fig. 6. It is possible that a part of these heterocyclic ring containing $\text{—}\overset{\text{O}}{\parallel}\text{C—N—}$ or $\text{—}\overset{\text{O}}{\parallel}\text{C—O—}$ linkage may be cleaved as the polymerization

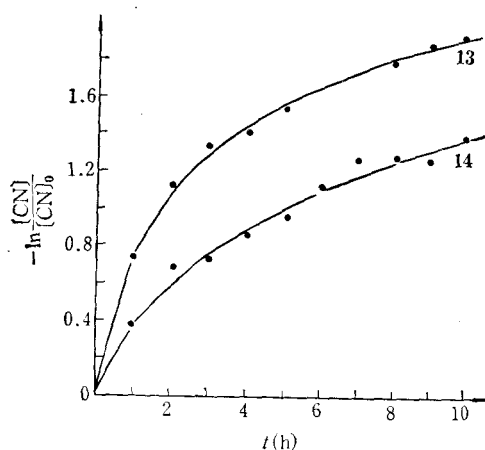


Fig. 6 Correlation between $-\ln \frac{[\text{CN}]}{[\text{CN}]_0}$ and time of polymerization of **13** and **14**

Table 2 Polymerization rate constants of heterocyclic dinitriles

Dinitrile	Polymerization rate constant
	$k \times 10^4$ ($\text{l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$) at 300°C
5	3.083
6	1.608
7	2.633
8	5.361 (340°C)
9	3.972
10	5.139
11	5.389 (340°C)
12	3.556
12	7.500 (340°C)

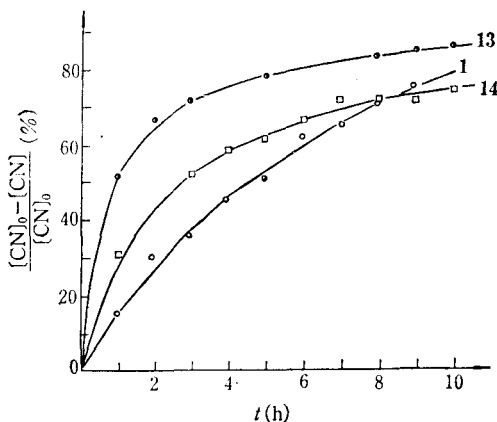
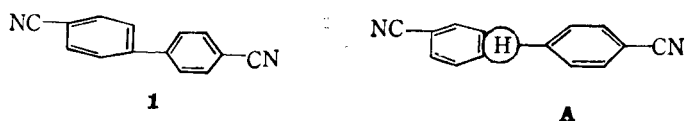


Fig. 7 Conversion of cyano group of dinitriles 13 and 14

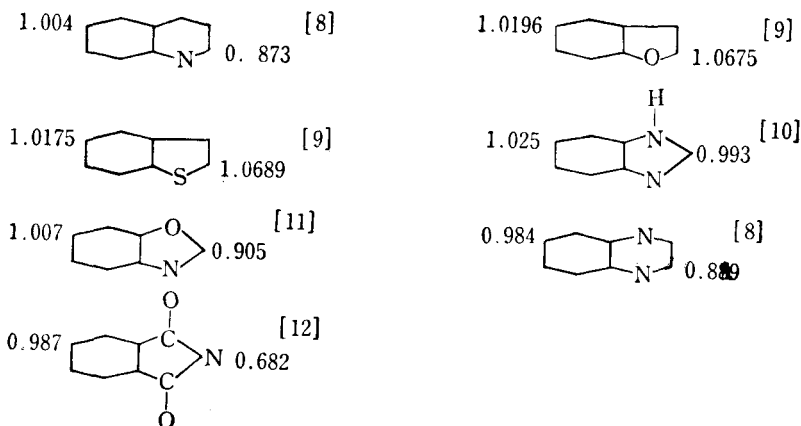
proceeded, so as to consume some amount of zinc chloride, therefore the polymerization rate decreases gradually. But from the conversion of cyano group as shown in Fig. 7, the polymerization rate of 13 is much faster than that of 1, especially at the beginning, and that of 14 is also faster than that of 1.

The polymerization rate constants of heterocyclic dinitriles are summarized in Table 2.

In order to elucidate the correlation of polymerization rate and structure of these ten heterocyclic dinitriles as compared with 1, we may consider that one benzene ring in 1 is substituted by the benzo-heterocyclic ring as 1 and A. Since



the π -electron density of the most of the above benzo-heterocyclic ring has been calculated by quantum chemistry, therefore the correlation can be explained on this base. Some relevant data cited from the literature are listed here. It can only be used for reference.



From these data it shows that the π -electron density on the 5- or 6-position which bears a cyano group is nearly the same, but on the 2-position which bears a cyano-phenyl group, the π -electron is quite different. As mentioned above, an electron withdrawing group in the para position of cyano group can accelerate the polymerization, a value lower than one in this position means electron deficiency as compared with benzene ring and this benzo-heterocyclic ring may look upon as an electron withdrawing group. Otherwise, benzo-heterocyclic ring with a value higher than one in this position may look upon as an electron donating group. Based on this consideration, we can explain why the polymerization rate of dinitrile 5,9 and 13 is faster than that of 1, and that of 6 is slower.

But there are two more problems. The first is that the polymerization rate of dinitriles containing only nitrogen as hetero atom is always lower than that deduced from calculation. It is possible that the nitrogen atom can more easily coordinate with Lewis acid, therefore the catalytic ability of zinc chloride decreased. The second problem is that the polymerization rate of dinitriles containing sulfur as hetero atom is always faster than that deduced from calculation, it deserves further consideration and investigation.

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