

AROMATIC AND HETEROCYCLIC DINITRILES AND THEIR POLYMERS

XIII. POLYMERIZATION KINETICS OF BENZO- NITRILE AND THE STRUCTURE OF PRODUCTS

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ABSTRACT

The polymerization kinetics of benzonitrile were studied, and the formation rate constants of s-triazine structure and linear polymer were determined. The influence of polymerization temperature and the amount of zinc chloride as catalyst on the ratio of linear to cyclic structure were also investigated, and the obtained results were discussed.

Aromatic and heterocyclic dinitriles can be polymerized to a crosslinked polymer containing s-triazine ring in main chain in the presence of Lewis acid catalyst. These polymers possess excellent thermostability. The syntheses of aromatic and heterocyclic dinitriles and their polymerization kinetics have been studied by the authors^[1-4]. It is difficult to study the structure of polymers, because they are insoluble and infusible. The determination of structure of polymers has been made by means of infrared spectroscopy. The disappearance of absorption peak of cyano group and the appearance of new characteristic strong absorption peak of s-triazine in the region of 1510, 1360 and 820 cm^{-1} ^[3] in infrared spectra indicate that the cyano group cyclotrimerized to s-triazine. It is only a qualitative consideration, because the linear polymer with $(-\text{C}=\text{N}-)$ conjugated double bond could be also formed from nitriles besides cyclotrimerization to s-triazine. Therefore, it is necessary to make a further study of the structure of polymers. In order to avoid the difficulty due to insolubility and infusibility of the polymer of dinitrile, benzonitrile was taken as model compound.

EXPERIMENTAL

The purified benzonitrile was mixed with a definite amount of zinc chloride and heated under controlled temperature for a certain period, according to the literature^[4]. The concentration of 2,4,6-triphenyl-1,3,5-triazine in the reaction mixture was determined by UV spectroscopy. The absorption at 270 nm was chosen as quantitative determination. The working curve is shown in Fig.1. The interference of the absorption of benzonitrile at this wave length could be corrected by the subtraction method, and the presence of linear polymer had no interference to this determination. The concentration of unreacted benzonitrile was determined by the weighing method.

UV spectrum was recorded with a SPECORD UV VIS spectrometer, and cyclohexane was used as solvent. The weighing method is that the sample was treated at 80°C and 1—2 mm Hg for 6 hours,

and the weight difference before and after the treatment was taken as the quantity of unreacted benzonitrile.

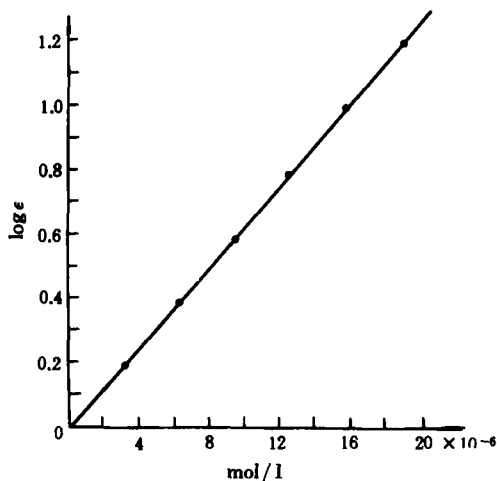


Fig.1 Working curve for determination of the concentration of 2,4,6-triphenyl-1,3,5-triazine by UV spectroscopy

RESULTS AND DISCUSSION

The polymerization kinetics of 4,4'-biphenyldicarbonitrile has been studied by us^[4], and the polymerization rate can be expressed as follows:

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

here $k' = k[\text{complex}]$

The polymerization kinetics of benzonitrile catalyzed by zinc chloride is also in accordance with this expression and the polymerization rate can also be calculated by formula (1) (see Fig.2). The cyano group of benzonitrile can either cyclotrimerize to s-triazine structure or polymerize to linear polymer. The formation rate of s-triazine structure can be denoted by

$$\frac{d[C]}{dt} = k'_1[CN] \quad (2)$$

and the formation rate of linear polymer can be denoted by

$$\frac{d[L]}{dt} = k'_2[CN] \quad (3)$$

Integrating formulas (1), (2) and (3), we can obtain:

$$k'_1 = \frac{k'[C]}{[CN]_0 \cdot (1 - e^{-k't})} \quad (4)$$

$$k'_2 = \frac{k'[C]}{[CN]_0 \cdot (1 - e^{-k't})} \quad (5)$$

$$\text{and } k_1 = k'_1/[cat.], k_2 = k'_2/[cat.], k = k_1 + k_2$$

k , k_1 and k_2 are the polymerization rate constant of cyano group, rate constant of triphenyl-s-triazine formation and the rate constant of linear polymer formation, respectively. Therefore, k , k_1 and k_2

may be calculated provided that the concentration of cyano group $[CN]$ and the concentration of 2,4,6-triphenyl-1,3,5-triazine $[C]$ can be determined.

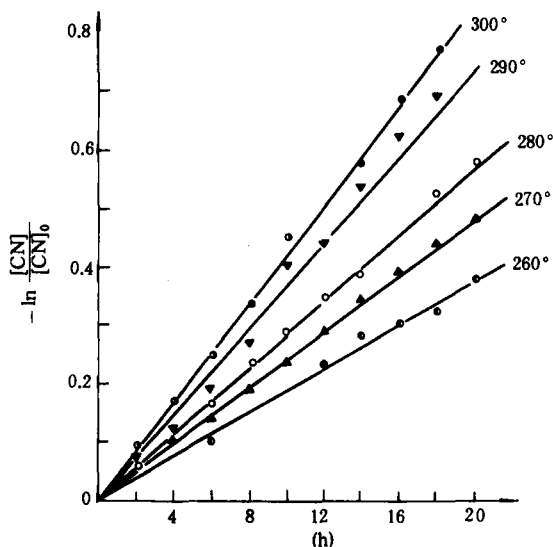


Fig.2 The correlation between $-\ln [CN]/[CN]_0$ and time

The influence of temperature on the ratio of linear to cyclic structure

The polymerization of benzonitrile catalyzed by zinc chloride (molar ratio of benzonitrile to zinc chloride is 1:0.04) was studied. The plot of $-\ln [CN]/[CN]_0$ with time is shown in Fig.2. The polymerization rate constants at different temperature are listed in Table 1. Compared with the polymerization rate constants of 4,4'-biphenyldicarbonitrile at the same condition^[4], the polymerization rate constants of benzonitrile are rather small. The activation energy obtained from Arrhenius plot (Fig.3) is 53.2 KJ/mol and the frequency factor is $1 \times 10^4 \text{ l.mol}^{-1} \text{ h}^{-1}$. Similar to the polymerization of other aromatic dinitriles studied by us^[5], this low activation energy and low frequency factor are characteristics to the polymerization of aromatic nitriles.

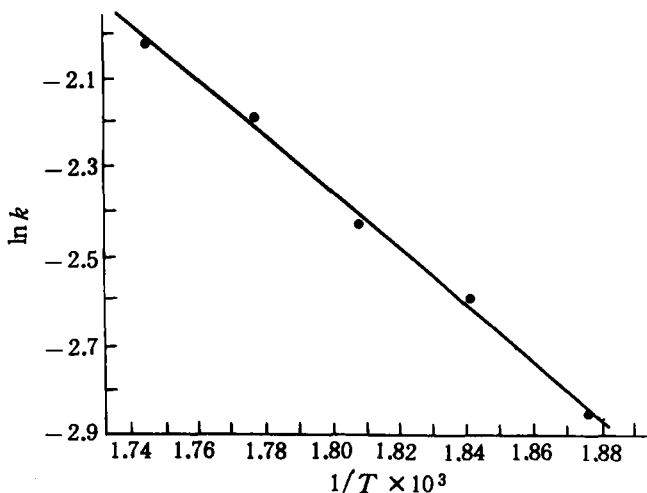


Fig.3 The Arrhenius plot of polymerization of benzonitrile

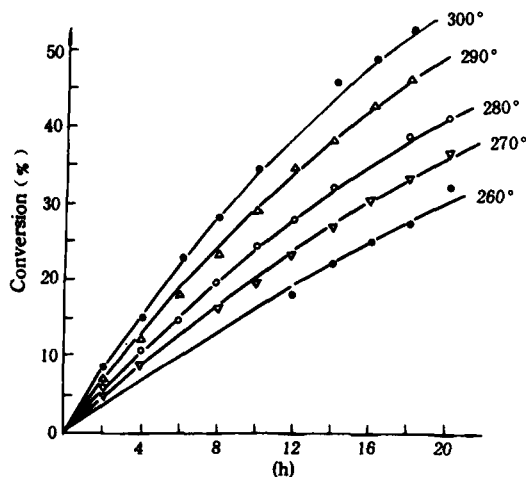
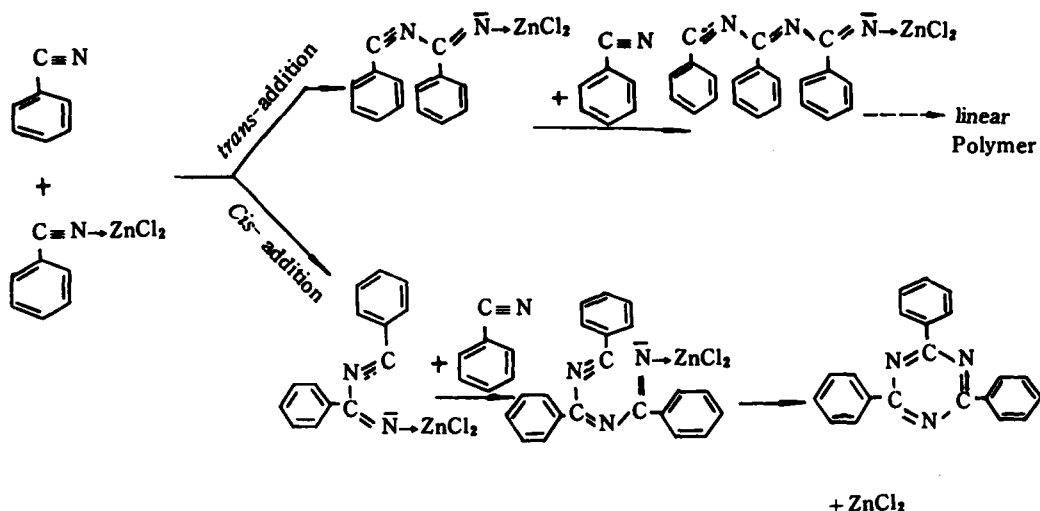


Fig.4 The formation rate of 2,4,6-triphenyl-1,3,5-triazine versus time

The formation rate of 2,4,6-triphenyl-1,3,5-triazine determined by UV spectroscopy is shown in Fig.4. The k_1 and k_2 calculated by formulas (4) and (5), and the ratio of linear to cyclic structure are also shown in Table 1. From the data in Table 1, it is shown that the main product is 2,4,6-triphenyl-1,3,5-triazine through cyclotrimerization of benzonitrile in the presence of 4 mole percent of zinc chloride at 260° to 300°C. It is also shown that the cyclotrimerization is more favorable with the increase of temperature, and the linear polymer is only 1.4% at 300°C. This phenomenon can be probably explained by the two types of addition reaction, *cis*- and *trans*- addition reaction, expressed by the following scheme:



The syn-structure is obtained by the *trans*-addition, in which the phenyl groups are on the same side, while the anti-structure is obtained by the *cis*-addition with the phenyl groups on different side. Only in the latter case the cyclotrimerization can occur to form the 2,4,6-triphenyl-1,3,5-triazine. It is obvious that the steric hindrance of the former is larger than that of the latter. Therefore, the main product of polymerization of benzonitrile is 2,4,6-triphenyl-1,3,5-triazine in the presence of zinc chloride at low concentration, especially at high temperature.

Table 1 The polymerization rate constants and ratio of linear to cyclic structure
(benzonitrile: $\text{ZnCl}_2 = 1:0.04$ molar ratio)

	260°	270°	280°	290°	300°
k ($\text{L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$)	0.0576	0.0744	0.0881	0.113	0.133
k_1 ($\text{L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$)	0.0531	0.0698	0.0838	0.108	0.131
k_2 ($\text{L}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$)	0.0045	0.0046	0.0043	0.005	0.002
ratio of linear to cyclic structure (k_2/k_1)	0.085	0.066	0.052	0.045	0.014

The influence of the amount of catalyst on the ratio of linear to cyclic structure

The influence of the amount of catalyst on the yield of 2,4,6-triphenyl-1,3,5-triazine is rather large in polymerization of benzonitrile in the presence of Lewis acid. The polymerization of benzonitrile at 350°C with different amounts of boron trifluoride anisole complex as catalyst has been reported in literature^[6]. It is necessary to study further on the polymerization kinetics of benzonitrile in the presence of Lewis acid.

The polymerization of benzonitrile in the presence of different amounts of zinc chloride was studied. The quantities of reacted benzonitrile and formed 2,4,6-triphenyl-1,3,5-triazine were determined (Fig.5,6). k_1 and k_2 were calculated from these data.

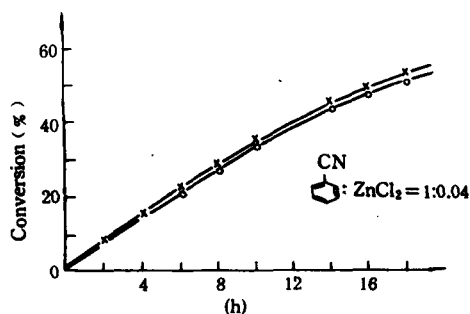


Fig.5 The reaction rate of benzonitrile and formation rate of 2,4,6-triphenyl-1,3,5-triazine versus time

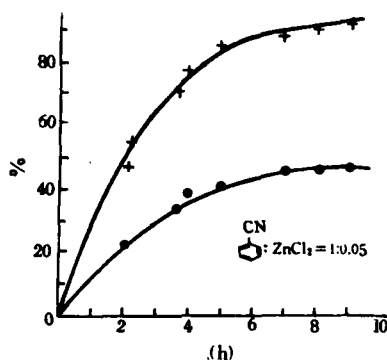


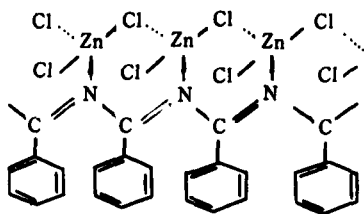
Fig.6 The reaction rate of benzonitrile and formation rate of 2,4,6-triphenyl-1,3,5-triazine versus time

From these figures, it is obvious that the polymerization is influenced by the amount of zinc chloride as catalyst. The quantity of the formed 2,4,6-triphenyl-1,3,5-triazine is almost equal to that of the reacted benzonitrile as 4 mole percent of zinc chloride used (Fig.5). But when the amount of zinc chloride is increased to 50 mole percent (Fig.6) the formed cyclotrimer is only 47% as benzonitrile is consumed up to 91%. It denotes that a rather large quantity of linear polymer is formed in this case. The k_1 , k_2 and the ratio of linear to cyclic structure using different amounts of zinc chloride are listed in Table 2.

Table 2 k_1 , k_2 and the ratio of linear to cyclic structure using different amounts of zinc chloride
(reaction temperature: 300°C)

ZnCl ₂ mole percent	4	12.5	25	50
k_1 (L·mol ⁻¹ ·h ⁻¹)	0.131	0.0725	0.0600	0.0437
k_2 (L·mol ⁻¹ ·h ⁻¹)	0.002	0.0241	0.0259	0.0363
Ratio of linear to cyclic structure (k_2/k_1)	0.014	0.33	0.43	0.83

From the data of Table 2, it is shown that the ratio of linear to cyclic structure increases with the increase of the amount of zinc chloride. It is probable that as the amount of zinc chloride is increased, the intermolecular chloride bridge can be formed between zinc chloride^[7]. The coordination of nitrogen atom of cyano group to this intermolecular bridged zinc chloride favors the formation of syn-structure during the polymerization of benzonitrile, and therefore, a larger quantity of linear polymer is formed. This is shown schematically as follows:



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