

AROMATIC AND HETEROCYCLIC DINITRILES AND THEIR POLYMERS XIV. STUDY ON THE CATALYSTS OF THE POLYMERIZATION OF AROMATIC NITRILES *

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ABSTRACT

Various catalysts for the polymerization of aromatic nitriles were investigated. It was found that Lewis acid-metal is a preferable catalyst system for the polymerization of aromatic nitriles and the polymerization rate is about 10 times faster than Lewis acid alone. The polymerization rate of benzonitrile catalyzed by Lewis acid and different metals was measured, and the activity of metals was in the following decreasing order, magnesium, zinc, sodium, calcium. Furthermore, the polymerization of benzonitrile catalyzed by different Lewis acid and zinc was also investigated.

Aromatic nitriles can be polymerized to a polymer containing aromatic and s-triazine ring in the main chain. The polymer has excellent thermal stability. Taking aromatic nitrile as capping agent of other polyheterocycles, such as polyimide, it is expected that the resin matrix for composite materials would have better thermal property at high temperature.

Up to date, there are two kinds of catalysts used for the polymerization of aromatic nitrile. One is protonic acid, such as chlorosulfonic acid^[1,2], p-toluene sulfonic acid^[3]. The other is Lewis acid^[4-6]. With chlorosulfonic acid as solvent, in the meantime as catalyst, the polymerization rate is higher, but the thermal stability of the polymer formed is not very good. The polymerization of aromatic nitriles using Lewis acid as catalyst has been thoroughly studied in our laboratory^[7,8], the polymer obtained possesses much better high temperature properties, but the polymerization rate is not high enough to satisfy the needs of the technology of capped polyimide for the preparation of composite materials. Therefore, it is necessary to find a more effective catalyst for the polymerization of aromatic nitriles. In this paper, we report some results of investigation on the catalysts for the polymerization of aromatic nitriles.

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EXPERIMENTAL

All the monomeric aromatic nitriles were purified by sublimation or distillation.

AlCl_3 was purified by sublimation. CoCl_2 and CuCl were dried at 130°C , and ZnCl_2 at 100°C in the presence of anhydrous hydrogen chloride gas under reduced pressure for 2 h.

The polymerization was carried out in sealed glass tube under controlled temperature ($\pm 0.1^\circ\text{C}$). The concentration of unreacted cyano group was measured by infrared spectroscopic analysis using potassium ferricyanide as internal reference in paraffin paste^[9]; while for the more volatile monomer, such as benzonitrile, the concentration of unreacted cyano group could be measured by weighing method, i.e., the weight loss at 100°C under 10 mmHg pressure for 3 h.

RESULTS AND DISCUSSION

1. Lewis acid–protonic compound system as catalyst for the polymerization of aromatic nitriles

The unpublished results in our laboratory showed that the polymerization rate of aromatic nitriles using Lewis acid as catalyst can be increased by the addition of some protonic compounds. The results of polymerization of benzonitrile catalyzed by cuprous chloride with the addition of some protonic compounds are listed in Table 1. It is shown that the addition of hydroquinone or benzoic acid is not so effective to accelerate the nitrile polymerization, and on the contrary, the polymerization rate is decreased by the addition of the strong acid, such as trifluoroacetic acid.

Table 1 The polymerization of benzonitrile catalyzed by different catalysts

Catalysts	$\text{C}_6\text{H}_5\text{CN} : \text{CuCl} :$ protonic compd. (molar ratio)	Conversion of cyano group (%)
CuCl	1 : 0.05	6.9
CuCl , hydroquinone	1 : 0.05 : 0.01	8.2
CuCl , hydroquinone	1 : 0.05 : 0.05	10.9
CuCl , benzoic acid	1 : 0.05 : 0.01	10.5
CuCl , benzoic acid	1 : 0.05 : 0.05	15.9
CuCl , CF_3COOH	1 : 0.05 : 0.01	2.7
CuCl , CF_3COOH	1 : 0.05 : 0.03	1.2

Temp.: 270°C ; Time: 10 h

The addition of water is more effective to accelerate the conversion of cyano group of benzonitrile catalyzed by cobaltous chloride. The results are shown in Fig. 1. Further studies showed that hydrolysis of benzonitrile to benzamide was simultaneously occurred with the nitrile polymerization in the presence of water, as the

results indicated in Table 2. The quantity of the benzamide formed was increased with increasing of the amount of water added, but the conversion of cyano group reached maximum at the molar ratio of cobaltous chloride to water at 1 : 6 .

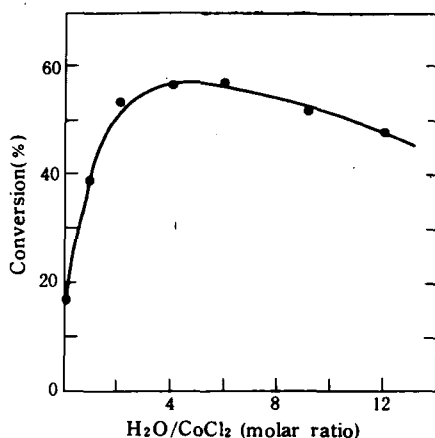


Fig. 1 Conversion of cyano group of benzonitrile in the presence of CoCl₂ and water
monomer : CoCl₂ = 1 : 0.05 molar ratio ;
Temp. : 270 °C ; time: 10 h.

Table 2 Influence of water on the conversion of cyano group of benzonitrile

CoCl ₂ /H ₂ O (molar ratio)	Conversion of cyano group (%)	Polymer/Amide (%)
1:0	16.8	100/0
1:1	38.9	96.2/3.8
1:2	53.9	91.1/8.9
1:4	56.4	84.2/15.8
1:6	56.7	67.0/33.0
1:9	51.6	50.0/50.0
1:12	48.4	44.1/55.9

CoCl₂ as catalyst; monomer/CoCl₂ : 1/0.05 molar ratio ; Temp. : 270 °C ; time : 10 h .

The hydrolyzed product was separated by sublimation, and the melting point (129 — 30 °C) and infrared spectrum (with characteristic band at 3360, 3160, 1655 and 1620 cm⁻¹) of sublimate were identical with the authentic benzamide sample.

The formation of amide was also confirmed by the polymerization of p - chlorobenzonitrile and 4, 4' - biphenyldicarbonitrile catalyzed by cobaltous chloride with the addition of water. The characteristic absorption bands were shown in infrared spectra at 3360, 3170, 1690, 1655 cm⁻¹ and 3390, 3140, 1655 cm⁻¹ respectively.

Furthermore, the polymerization of p - chlorobenzonitrile catalyzed by cuprous chloride was also studied by DTA method. The results are shown in Fig. 2. In the absence of water, the DTA spectrum showed only one exothermal peak, while in the

addition of water, another exothermal peak of formation of amide appeared in the DTA spectrum, and this second exothermal peak became larger as the amount of water increased.

From the above results, we come to conclusion that Lewis acids with the addition of protonic compounds including water are not an effective and suitable catalyst system for the polymerization of aromatic nitriles.

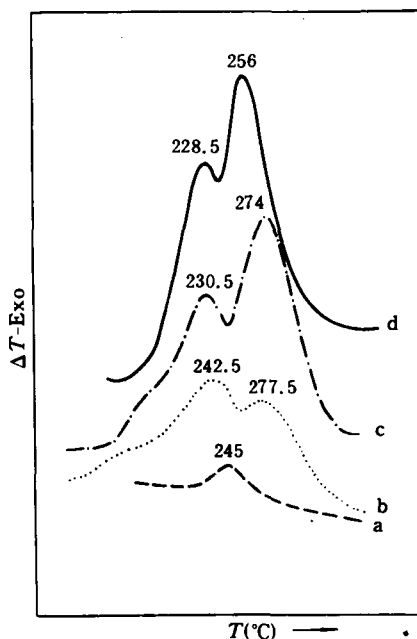


Fig. 2 Effect of water on the polymerization of *p*-chlorobenzonitrile catalyzed by cuprous chloride DTA at 10 °C/min. in sealed tube; monomer/CuCl : 1/0.5 molar ratio; a, b, c, d — the molar ratio of H₂O/CuCl is 0, 0.5, 1, 2 resp.

2. Lewis acid-metal system as catalyst for the polymerization of aromatic nitrile

It has been reported in the patent literature^[10] that transition metal halide with a reducing substance, such as zinc, sodium borohydride etc., can be used as catalyst for the polymerization of diene. Similarly, we try to use cobaltous chloride and a metal whose electronegativity value is less than 1.6 as catalyst system for the polymerization of aromatic nitriles. The results of polymerization of benzonitrile catalyzed by cobaltous chloride with a metal, together with catalyzed by metal alone for comparison are listed in Table 3. From these results, it is indicated that the conversion of cyano group of benzonitrile catalyzed by cobaltous chloride increases obviously with the addition of metal, especially magnesium or zinc. However, magnesium or zinc alone has no catalytic effect for polymerization of benzonitrile at all.

The comparison of polymerization rate of benzonitrile catalyzed by Lewis acid-metal system or Lewis acid alone is shown in Fig. 3. It is obvious that Lewis acid-metal system has much higher catalytic activity for nitrile polymerization. From this figure we can also see that the polymerization rate of benzonitrile catalyzed by Lewis acid-metal system is directly proportional to the first order of cyano group concentration, and the rate equation can be expressed as follows:

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

Table 3 The conversion of cyano group of benzonitrile catalyzed by different catalysts

Catalyst	Conversion (%)	Catalyst	Conversion (%)
CoCl ₂ , Mg	32.40	Mg	0
CoCl ₂ , Zn	29.94	Zn	0
CoCl ₂ , Na	26.98	Na	23.12
CoCl ₂ , Ca	24.53	Ca	4.03
CoCl ₂ , NaBH ₄	16.16	NaBH ₄	10.25
CoCl ₂	4.84		

Temp.: 260 °C; Time: 10 h

monomer : CoCl₂ : metal = 1 : 0.05 : 0.05 molar ratio

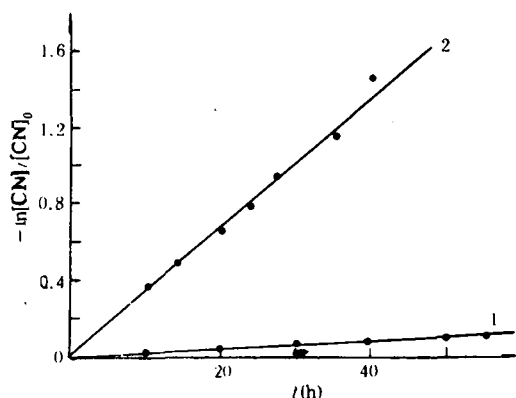


Fig. 3 The rates of polymerization of benzonitrile catalyzed by CuCl (1); CuCl and Zn (2)

Temp.: 270 °C; monomer/CuCl : 1/0.05 molar ratio; monomer/CuCl/Zn : 1/0.05/0.05 molar ratio.

The polymerization of other three nitriles catalyzed by cuprous chloride–zinc system or cuprous chloride alone was also carried out. The results are listed in Table 4, in which k_1' and k_2' denote the apparent polymerization rate constants catalyzed by cuprous chloride or cuprous chloride–zinc, respectively.

Table 4 Polymerization rate constants of nitriles catalyzed by cuprous chloride (k_1'); cuprous chloride and zinc (k_2')

Monomer	k_1' (h ⁻¹)	k_2' (h ⁻¹)
benzonitrile	0.0021	0.033
p-chlorobenzonitrile	0.033	0.266
p-cyanobenzoic acid	0.046	0.153
4,4'-biphenyldicarbonitrile	0.012	0.083

Temp.: 270 °C;

monomer/CuCl : 1/0.05 molar ratio;

monomer/CuCl/Zn : 1/0.05/0.05 molar ratio.

The results of polymerization of benzonitrile catalyzed by four Lewis acids alone and with metal zinc are shown in Fig. 4 and 5, respectively. The polymerization rate constants are summarized in Table 5. It indicates that the catalytic activity order sequence of the two series of catalyst system for the polymerization of benzonitrile are different.

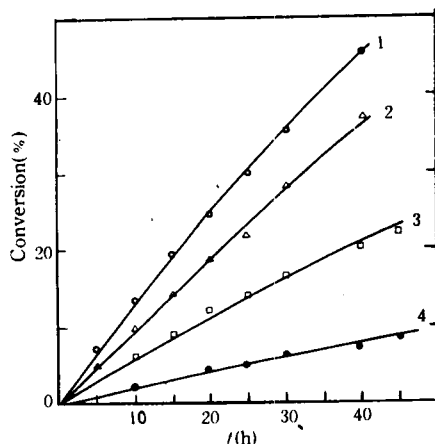


Fig. 4 The conversion of benzonitrile catalyzed by four Lewis acids

Temp.: 270 °C ;
monomer : Lewis acid = 1 : 0.05
molar ratio. 1 - ZnCl_2 ; 2 - CoCl_2 ;
3 - AlCl_3 ; 4 - CuCl

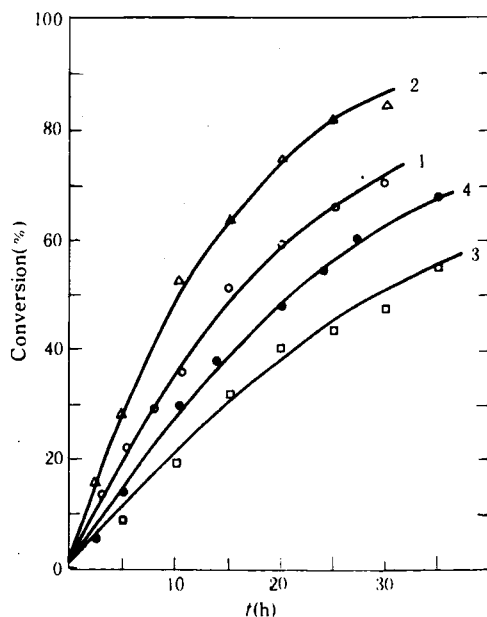


Fig. 5 The conversion of benzonitrile catalyzed by zinc and four Lewis acids

Temp.: 270 °C ;
monomer : Lewis acid : Zn = 1 : 0.05 : 0.05
molar ratio : 1 - ZnCl_2 ; 2 - CoCl_2 ; 3 - AlCl_3 ; 4 - CuCl

Table 5 The apparent polymerization rate constants of benzonitrile catalyzed by different catalysts

Catalysts	k' (h^{-1})	Catalysts	k' (h^{-1})
ZnCl_2	0.0146	ZnCl_2, Zn	0.0447
CoCl_2	0.0110	CoCl_2, Zn	0.0684
AlCl_3	0.00620	AlCl_3, Zn	0.0238
CuCl	0.00211	CuCl, Zn	0.0325

Temp.: 270 °C ; Monomer : Lewis acid (: metal) = 1 : 0.05 (: 0.05) molar ratio

From the above results, we can conclude that Lewis acid-metal is a preferable catalyst system for the polymerization of aromatic nitriles, and we may predict that the polymerization of aromatic nitriles could proceed in a reasonable rate at somewhat lower temperature, such as around 250 °C.

Keywords :

Aromatic nitrile ; Catalyst ; Polymerization.

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