

Note

POLYMERIZATION OF ACRYLONITRILE WITH ORGANOLANTHANIDES AS SINGLE-COMPONENT CATALYSTS*

Lai-qiang Ying, Xiao-wei Ba, Yu-ying Zhao, Gang Li, Tao Tang and Ying-tai Jin**
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

Abstract $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$ and $\text{Ind}_2\text{LnN}(i\text{-Pr})_2$ ($\text{Ln} = \text{Y}, \text{Yb}$) were used as a single-component catalyst for the polymerization of acrylonitrile (AN) respectively. The regularity of polymerization of AN and stereoregularity of polyacrylonitrile (PAN) were also studied in both cases. Both catalysts can produce PAN with molecular weight from 10,000 to 30,000. In addition, the catalytic activity and molecular weights were increased by the addition of PhONa .

Keywords Acrylonitrile, Organolanthanide, Polymerization

INTRODUCTION

Polyacrylonitrile (PAN) is a fiber-forming polymer and becomes an important material in the textile industry. The polymerization of acrylonitrile has been mainly carried out by radical initiators and anionic initiators. In the radical polymerization, it is usually initiated by $\text{K}_2\text{S}_2\text{O}_8\text{-Na}_2\text{S}_2\text{O}_5$ ^[1, 2], $\text{Fe}^{2+}\text{-H}_2\text{O}_2$ ^[3, 4], benzoyl peroxide and 2,2'-azobis(isobutyronitrile)^[5]. Compared with the radical polymerization, anionic polymerization can produce high stereoregular polyacrylonitrile. So anionic polymerization was studied in detail. In 1948, Beaman first reported the anionic polymerization of acrylonitrile^[6]. Recently, Kamide *et al.* reported that highly syndiotactic polyacrylonitrile can be obtained with BeR_2 or MgR_2 as initiator, but their activity is very low^[7, 8]. The polymerization of acrylonitrile with organolanthanides as single-component catalysts was rarely reported. Recently, Mao reported that lanthanocene amides can polymerize acrylonitrile effectively with some additives^[9], but the catalytic activity is quite low. In this article, we demonstrate that $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$ and $\text{Ind}_2\text{LnN}(i\text{-Pr})_2$ ($\text{Ln} = \text{Y}, \text{Yb}$) exhibit relatively high catalytic activity in the polymerization of AN.

EXPERIMENTAL

Materials

Acrylonitrile (AN) was distilled over calcium hydride powder and stored over molecular sieves under argon. Toluene, THF and other solvents (analytical grade) were dried and freed from oxygen by refluxing over Na/K alloy and distilled under argon before use. $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$ and $\text{Ind}_2\text{LnN}(i\text{-Pr})_2$ ($\text{Ln} = \text{Y}, \text{Yb}$) were synthesized according to Refs. [10] and [11], respectively.

Polymerization of AN

All polymerization reactions were performed under dry argon. A typical example is given as follows. AN (40 mmol, 2.63 mL) was added to a toluene solution (4 mL) of $(\text{C}_9\text{H}_7)_2\text{LnN}(i\text{-Pr})_2$ (0.08 mmol, 0.02 mol/L) with

* The project is supported by the State Key Laboratory of Polymer Physics and Chemistry in Chinese Academy of Sciences and the Joint Foundation of Polymer Chemistry Laboratory of Chinese Academy of Sciences and the China Petro-Chemical Corporation.

** Corresponding author: Ying-tai Jin (金鹰泰), E-mail: ytjin@ciac.jl.cn

Received April 7, 2000

vigorous magnetic stirring at the desired temperature. After the polymerization had proceeded for a given time, the solution was poured into ethanol containing 5% HCl solution (50 mL). The resulting polymer was washed three times with ethanol and dried in vacuum at 50°C.

Measurements

The intrinsic viscosity of PAN was determined in *N,N*-dimethyl formamide (DMF) solution at 25°C using a viscometer and molecular weight of the PAN was calculated from the following formula:

$$[\eta] = 2.09 \times 10^{-4} M_v^{0.76} \text{ (DMF, 25°C)}$$

NMR spectra of the polymers were taken on a Unity-400 spectrometer in DMSO-*d*₆ as solvent.

RESULTS AND DISCUSSION

Tables 1 and 2 summarized the results of AN polymerization using catalysts $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$, $\text{Ind}_2\text{LnN}(\text{i-Pr})_2$ (Ln = Y, Yb) at various temperatures and catalyst concentrations, respectively. All three catalysts appeared to have considerably high catalytic activity. Higher polymerization temperature is necessary to obtain higher activities. It is noteworthy that the catalyst systems with the addition of PhONa can increase the activity and molecular weight of PAN. However, PhONa alone shows no activity in the polymerization of AN. So, the increase of activity and molecular weight of PAN with the addition of PhONa to the catalyst system is probably due to the fact that the catalyst has been stabilized by PhONa.

Table 1. Polymerization of AN with $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$

Polym. Temp. (°C)	[AN]/[Cat]	[PhONa]/[Cat]	Conversion (%)	$M_v (\times 10^{-4})$
0	500	-	9	0.78
0	300	-	36	1.02
25	500	-	29	0.84
50	500	-	36	1.01
50	300	-	54	0.78
50	300	3	83	1.95

Polymerization condition: solvent = toluene; [AN] = 7.6 mol/L; *t* = 5 h

Table 2. Polymerization AN with $\text{Ind}_2\text{LnN}(\text{i-Pr})_2$ (Ln = Y, Yb)

Catalyst	Polym. Temp. (°C)	[AN]/[Cat]	[PhONa]/[Cat]	Conversion (%)	$M_v (\times 10^{-4})$
$\text{Ind}_2\text{YN}(\text{i-Pr})_2$	0	500	-	20	2.91
$\text{Ind}_2\text{YN}(\text{i-Pr})_2$	0	300	-	32	1.15
$\text{Ind}_2\text{YN}(\text{i-Pr})_2$	20	500	-	38	1.41
$\text{Ind}_2\text{YN}(\text{i-Pr})_2$	20	300	-	46	1.06
$\text{Ind}_2\text{YN}(\text{i-Pr})_2$	50	300	-	64	0.89
$\text{Ind}_2\text{YN}(\text{i-Pr})_2$	50	300	3	76	1.32
$\text{Ind}_2\text{YN}(\text{i-Pr})_2$	50	300	5	75	1.31
$\text{Ind}_2\text{YbN}(\text{i-Pr})_2$	0	500	-	21	1.75
$\text{Ind}_2\text{YbN}(\text{i-Pr})_2$	20	500	-	36	1.65

Polymerization condition: solvent = toluene; [AN] = 5.1 mol/L; *t* = 5 h

The influence of monomer concentration on polymerization activity has also been investigated using $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$ and $\text{Ind}_2\text{YN}(\text{i-Pr})_2$ as single-component catalysts, respectively. The results are shown in Figs. 1 and 2. It can be seen that the activity of catalysts increases with increasing monomer concentration, but the molecular weight remains steady with $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$ as catalyst and it decreases slightly with $\text{Ind}_2\text{YN}(\text{i-Pr})_2$ as catalyst.

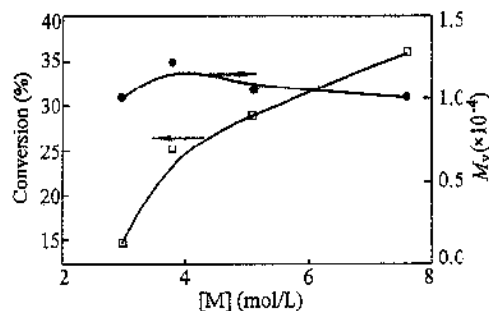


Fig. 1 The effect of monomer concentration on polymerization using $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$ as catalyst
Polym. cond.: $[\text{AN}]/[\text{cat}] = 500 \text{ mol/mol}$, $T = 50^\circ\text{C}$,
 $t = 5 \text{ h}$

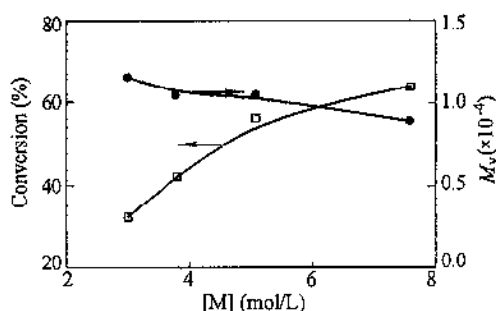


Fig. 2 The effect of monomer concentration on polymerization using $\text{Ind}_2\text{YN}(i\text{-Pr})_2$ as catalyst
Polym. cond.: $[\text{AN}]/[\text{cat}] = 300 \text{ mol/mol}$, $T = 50^\circ\text{C}$,
 $t = 5 \text{ h}$

Table 3. The stereoregularity of PAN

Catalyst	Tacticity(%)		
	<i>mm</i>	<i>mr</i>	<i>rr</i>
$\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$	25	32	43
$\text{Ind}_2\text{YN}(i\text{-Pr})_2$	29	36	35

The stereoregularity of PAN was determined by ^{13}C -NMR (Table 3); the results show that the resulting polymers are all random^[12].

CONCLUSIONS

It has been found that $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$, $\text{Ind}_2\text{LnN}(i\text{-Pr})_2$ ($\text{Ln} = \text{Y}, \text{Yb}$) complexes are able to act as new kinds of effective initiators for polymerization of AN. The influence of the temperature, initiator concentration, monomer concentration on polymerization activity of PAN has been investigated.

REFERENCES

- 1 Stamicarber, B.V., 1984, E. Pat., 0144793
- 2 Saker, S., Adhikari, M.S., Benejee, M. and Konar, R.S., J. Appl. Polym. Sci., 1988, 36: 1865
- 3 Dainton, F.S., Seaman, P.H., James, D.G.L. and Eaton, R.S., J. Polym. Sci., 1959, 34: 26
- 4 Dainton, F.S. and Seaman, P.H., J. Polym. Sci., 1959, 39: 279
- 5 Koningsberger, Sutomen, J. Polym. Sci., 1964, 1: 200
- 6 Beaman, R.G., J. Am. Chem. Soc., 1948, 70: 3115
- 7 Nakano, Y., Hisatani, K. and Kamide, K., Polym. Int., 1994, 34: 397
- 8 Nakano, Y., Hisatani, K. and Kamide, K., Polym. Int., 1995, 36: 87
- 9 Mao, L.S., "Doctoral thesis of Zhejiang University", Zhejiang University, 1997
- 10 Evans, W.J., Chamberlain, L.R., Ulibarri, T.A. and Ziller J.W., J. Am. Chem. Soc., 1988, 110: 6423
- 11 Mao, L.S. and Shen, Q., J. Polym. Sci., Part A, Polym. Chem., 1998, 36: 1593
- 12 Schaefer, J., Macromolecules, 1971, 4: 105