New Catalyst System, FeCl3-Et3-nAlCln (n=1, 2), for the Alternating Copolymerization of Butadiene-1,3 with Acrylonitrile

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ABSTRACT

Butadiene-1,3 and acrylonitrile were copolymerized by alkylaluminum halides and ferric chloride systems. The efficiency of the aluminum components of these systems appears to decrease in the following order: $Et_2AlCl >$ $EtAlCl_2 > Et_3Al$. Effective catalysts were not necessarily dependent on the mixing orders of the catalyst and monomers. It was found that different feed ratios between two monomers, which were varied over a wide range, always resulted in the formation of 1:1 copolymer. In order to investigate the initiation and propagation reactions, electron paramagnetic resonance was measured and a polarographic method was used on the reduction reaction of ferric chloride with organoaluminum halides in acetonitrile.

Several kinds of catalyst systems for alternating copolymerization of butadiene (BD) and acrylonitrile (AN) have been claimed in recent years [1-3]. The most effective catalyst system was $EtAlCl_2$-$VOCl_3$, and kinetic data have shown that the BD-AN-Al complex was formed

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and polymerized to alternating copolymer, but initiation and propaga-
tion species were not clear [4]. We tried the polymerization of
butadiene with acrylonitrile by several Lewis acids, $SbCl_5$, BF_3OEt_2,
and $FeCl_3$, combined with organoaluminum halides. It was found that
$FeCl_3$-$Et_{3-n}AlCl_n$ was fairly active and could produce high molecular
weight alternating copolymer. In these catalyst systems ferric chlor-
ide and diethylaluminum chloride were shown to possess the most
effective catalytic activity, and this result was different from the
$Et_{3-n}AlCl_n$-$VOCl_3$ system, in which $EtAlCl_2$-$VOCl_3$ was shown to
have the highest catalytic activity [1].

It seems that the catalytic activity depends both on the reduction
reaction of transition metal by organoaluminum halides and the con-
centration of the BD-AN-Al complex. Some characteristic results
were obtained by the measurement of electron paramagnetic resonance
of ferric chloride in the polymerization system, and the reduction
reaction of ferric chloride in catalytic systems was followed by a
polarographic method.

EXPERIMENTAL

Catalyst Components

Triethylaluminum obtained from Texas Alkyl, Inc. was used with-
out further purification. Diethylaluminum chloride obtained from
Ethyl Corp. was distilled under reduced pressure, bp 110°C (30 Torr).
Ethylaluminum dichloride was prepared from 1 mole of triethylalumi-
num and 2 moles of aluminum trichloride by mixing, reacting at 130°C
and distilling under reduced pressure, bp 104°C (34 Torr). Ferric
chloride was purified by sublimation of commercial anhydrous ferric
chloride in a dry nitrogen atmosphere.

Monomer

Butadiene obtained from Japanese Geon Co. was purified under dry
nitrogen gas by the usual method. Acrylonitrile was refluxed under
calcium hydride and distilled before use.

Solvent

Solvents were of reagent grade and were purified by ordinary
methods.

Copolymerization

In a 50-ml dry glass ampoule flushed with a stream of purified nitrogen were placed 2.5 ml of toluene as solvent and 3.2 ml (0.05 mole) of acrylonitrile in which 0.081 g (0.5 mmole) of ferric chloride was dissolved. After the solution had been cooled at -78°C, 4 mmoles of diethylaluminum chloride in 2.5 ml toluene was added and 3.9 ml (0.05 mole) of liquid butadiene was distilled into this mixture. The ampoule was sealed and dipped in a thermostat at constant temperature.

The polymerization was stopped by methanol and the polymer was dissolved in dimethyl formamide. Purified polymer was precipitated by pouring the dimethyl formamide solution into methanol containing a small amount of hydrochloric acid and phenyl-β-naphthylamine, and dried in vacuo.

Polymer Characterization

Nuclear magnetic resonance spectra were recorded by a 100 Hz high resolution NMR spectrometer Model JNM-4H-100 of the Japan Electron Optics Lab. Co. The deuterochloroform solution of the polymer containing tetramethylsilane as the internal standard was sealed in Pyrex tube of 5 mm diameter. Infrared measurements of the copolymer were carried out with a Hitachi Co. Model EPI-S2 infrared spectrometer.

Composition of the copolymers was determined by the elemental analysis of nitrogen with a Yanagimoto Co. Model MT-1 CHN Corder.

The intrinsic viscosity of the polymers was measured in dimethyl formamide at 30°C by the use of a Ubbelohde-type viscometer.

EPR Measurement of Reaction Systems

Electron paramagnetic resonance spectra were recorded by a TE_{102} resonant cavity of an X band ESR spectrometer, Japan Electron Optics Lab. Co. Model JES-ME-2X. Mixtures of catalyst, monomer, and solvent were prepared at -78°C by the method described above. The solution was sealed under dry nitrogen gas in Pyrex tubes designed to fit directly into the microwave resonant cavity. The g values were determined with the aid of a standard sample of tetra-cyanoquinodimethane lithium complex (TCNQ-Li) which has a g factor of 2.003. It was measured from -150 to 30°C.

Polarography of $FeCl_3$-Et_{3-n} $AlCl_n$ in Acetonitrile

A polarogram was recorded on a Yanagimoto Co. high sensitive polarograph Model PA-201. A solution of 0.081 g (0.5 mmole) of ferric chloride in 0.1 mole of acetonitrile and one of 4 mmoles of diethylaluminum chloride in 12 ml of toluene were prepared separately at -78°C and reacted at 30°C. Then the reduction of ferric chloride was begun and the reaction mixtures were quenched after various time intervals by sampling a portion of the solution by adding it to methanol. The concentration of the remaining ferric chloride was determined by the polarographic method. The solution was diluted with acetonitrile at a concentration of 10^{-4} mole/l of ferric chloride. With sodium perchlorate as supporting electrolyte, ferric chloride in acetonitrile exhibited two well-defined reduction waves corresponding to the reduction of Fe(III) to Fe(II) and to Fe(0), respectively. The quenched solvent did not disturb the polarographic measurement, diffusion currents being well proportional to the concentration of ferric chloride between 10^{-4} and 10^{-5} mole/l.

RESULTS AND DISCUSSION

Copolymerization of Butadiene with Acrylonitrile

Results of butadiene and acrylonitrile copolymerization reaction with $FeCl_3$-$Et_{3-n}AlCl_n$ are shown in Table 1. Halogen is necessary for the aluminum compounds to serve as copolymerization catalyst, and diethylaluminum chloride in combination with ferric chloride was the most effective. The copolymer obtained by this system was chloroform soluble and had a high intrinsic viscosity. In the copolymerization with benzoyl peroxide (BPO) as initiator, some metal chlorides completely suppressed copolymerization. The copolymerization with BPO as initiator was completely suppressed by ferric chloride, but it was promoted by the alkylaluminum chloride.

The results of the copolymerization by the $FeCl_3$-$Et_{3-n}AlCl_n$ system at 0-30°C with various monomer feeds are shown in Table 2.

The rate of polymerization and the intrinsic viscosity of the copolymer obtained seem to be maximum when the feed ratio is 1:1. These results are similar to other alternating copolymerization catalytic systems in the polymerization of a donor-acceptor complex, that is, butadiene as donor monomer and acrylonitrile complexed with diethylaluminum chloride as acceptor monomer [5].

TABLE 1. Copolymerization between Butadiene and Acrylonitrile with $FeCl_3$ -$Et_{3-n}AlCl_n$ [a]

Run No.	Catalyst[b]	Mmoles	Temp. (°C)	Polym. time (hr)	Conversion (mole %)	Gel (%)	$[\eta]$	AN (mole %)
1	$Et_3Al/FeCl_3$	4/1	20	72	1.3			44.6
2	$Et_2AlCl/FeCl_3$	4/1	20	72	25.3	35	1.97	53.7
3	$EtAlCl_2/FeCl_3$	4/1	20	72	17.0	74	1.09	49.0
4	$Et_2AlCl/FeCl_3$	4/0.5	0	24	9.1	0	3.05	51.0
5	$EtAlCl_2/FeCl_3$	4/0.5	0	24	0.3			85.8
6	$BPO/FeCl_3$	1/0.5	20	24	0			
7	Et_2AlCl/BPO	4/1	20	24	28.0	0	1.32	45.7
8	$EtAlCl_2/BPO$	4/1	20	24	77.0	100		46.9

[a]Polymerization conditions: Butadiene 50 mmoles, acrylonitrile 50 mmoles, toluene 5 ml.
[b]BPO = benzoyl peroxide. catalyst systems were prepared at -78°C.

TABLE 2. Copolymerization between Butadiene and Acrylonitrile with $FeCl_3$-Et_2AlCl System at Various Feed Ratios[a]

Run No.	Butadiene in feed (mole %)	N %	Butadiene in copolymer (mole %)	Conversion (mole %)	$[\eta]$
9	12.5	14.75	44.6	3.2	0.51
10	25.0	14.74	44.7	3.9	0.81
11	50.0	12.81	51.0	9.1	3.05
12	75.0	12.76	51.2	5.5	2.90
13	87.5	13.01	50.2	3.0	2.75

[a]Polymerization conditions: Butadiene 50 mmoles, acrylonitrile 50 mmoles, Et_2AlCl 4 mmoles, $FeCl_3$ 0.5 mmoles, toluene 5 ml, 0°C, 24 hr.

Characterization of the Copolymers

Figure 1 shows an infrared spectrum of butadiene-acrylonitrile copolymer prepared by $FeCl_3Et_2AlCl$ catalyst at $0°C$. Some characteristic absorptions are observed at 2200 cm^{-1}, assigned to the nitrile group, and at 970 cm^{-1}, assigned to the trans-1,4 linkage of the butadiene unit. The absorption assignable to vinyl or cis-1,4 linkage of the butadiene unit is scarcely recognized. The NMR spectrum of the copolymer is shown in Fig. 2. It was found that diad methylene protons of the butadiene unit appeared at 7.9τ and methylene protons of the butadiene unit in butadiene-acrylonitrile diad was recognized at 7.7τ, and so the copolymer prepared by this catalyst has a high regularity of alternation in the polymer chain [5].
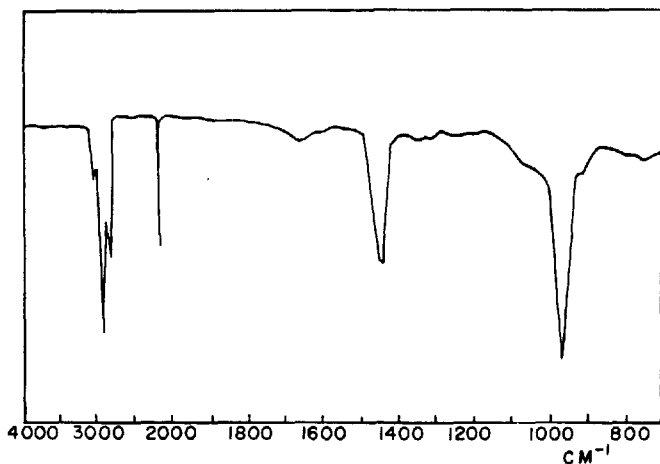

FIG. 1. Infrared spectrum of butadiene-acrylonitrile copolymer obtained with $FeCl_3$-Et_2AlCl.

Effects of the Order of Mixing of Catalyst Components and Monomers on the Copolymerization

It was reported that the copolymer yield had been markedly influenced by the order of mixing of the reagents for the polymerization reaction. When the transition metal halides and organoaluminum halides were mixed in the absence of acrylonitrile, catalytic activity
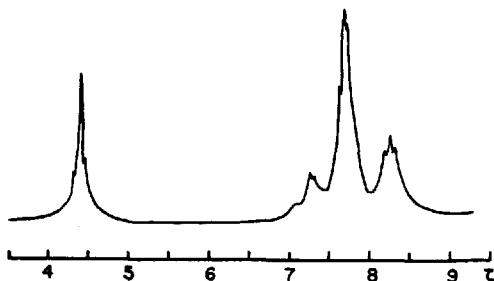
FIG. 2. NMR spectrum of butadiene-acrylonitrile copolymer.
Feed ratio, BD/AN, 12.5/87.5; copolymer AN mole %, 56; $CDCl_3$, 5%.

was extremely suppressed [5]. Various mixing orders have been ex-
amined at $-78°C$ in the copolymerization by $FeCl_3-Et_2AlCl$ catalyst.
The result is shown in Table 3. In this catalyst system, better results
were obtained when diethylaluminum chloride and ferric chloride are
mixed in the presence of acrylonitrile monomer. It is characteristic
for these two components to have a similar activity, that is, any de-
creases in the catalytic activity were not observed even after the two
components were aged for 30 min at room temperature in toluene.
The active species for the initiation seemed to be very stable compared
to the $VOCl_3$ system.

Effect of the Ratio of Catalyst Components on the
Polymerization Rate and Intrinsic Viscosity

Figures 3 and 4 show the dependency of the conversion and of the
intrinsic viscosity of the copolymers obtained upon the various concen-
trations of diethylaluminum chloride or ferric chloride at a given re-
action time. It is shown in Fig. 3 that the conversion and intrinsic
viscosity increase linearly with an increase in the initial concentration
of diethylaluminum chloride when the mole ratio of butadiene to
acrylonitrile is 1.
It is shown in Fig. 4 that the overall polymerization rate was ac-
celerated at the low concentration of ferric chloride, but the rate did
not appreciably increase after the mole ratio of ferric chloride over
diethylaluminum chloride reached 0.5. The intrinsic viscosity of
the copolymer markedly decreased with an increase in ferric chloride
concentration. This may be due to the termination reaction of active
species by excess ferric chloride [6].

TABLE 3. Effect of Mixing Order of Reagents at $-78°$ C in the Case of $FeCl_3-Et_2$ AlCl System on Polymerization of Butadiene and Acrylonitrile[a]

Run No.	Mixing order	Conversion (mole %)	$[\eta]$	Acrylonitorile (mole %)
14	Tol, Fe, BD, Al, AN	4.5	2.6	50.3
15	Tol, Fe, Al, BD, AN	5.0	2.3	51.5
16	Tol, Fe, AN, Al, BD	9.1	3.1	51.0
17	Tol, Fe, Al, AN, BD	10.3	4.0	51.3
18[b]	Tol, Fe, Al, AN, BD	9.5	2.2	51.0

[a]Polymerization conditions: BD 50 mmoles, AN 50 mmoles, Et_2AlCl 4 mmoles, $FeCl_3$ 0.5 mmole, toluene 5 ml, 0° C, 24 hr.

[b]$FeCl_3$ and Et_2AlCl were reacted for 30 min in toluene at room temperature.
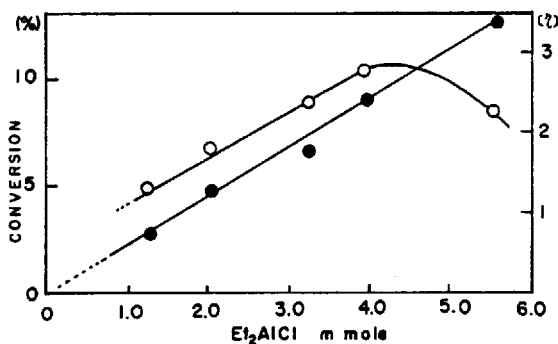
FIG. 3. Effect of Et_2AlCl on the conversion of polymerization and intrinsic viscosity. BD, AN, and $FeCl_3$ were 50, 50, and 0.5 mmoles, respectively. Toluene, 5 ml. 0° C, 12 hr. Open circles are intrinsic viscosity, filled circles are conversion.

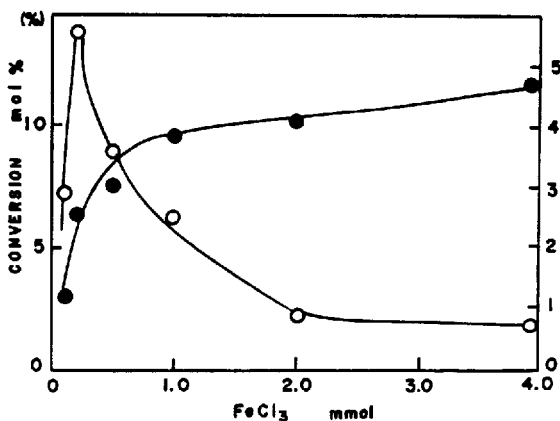FIG. 4. Effect of $FeCl_3$ on the conversion of polymerization and intrinsic viscosity. BD, AN, and Et_2AlCl were 50, 50, and 4 mmoles, respectively. Toluene, 5 ml. 0°C, 24 hr. Open circles are intrinsic viscosity, filled circles are conversion.

The dependency of the polymerization rate on temperature is shown in Figs. 5 and 6. In an early stage, polymerization proceeds as first-order with respect to the monomer concentration. From

Arrhenius plot of R_p vs $1/T$, the activation energy of overall polymerization is calculated to be 9.1 kcal/mole, the value being smaller than for the usual radical polymerization.
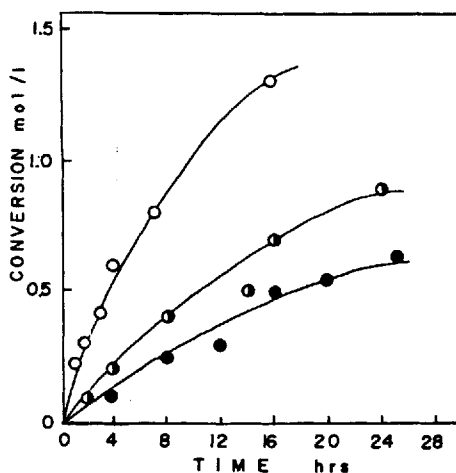

FIG. 5. Time-conversion curves of copolymerization. BD, AN, $FeCl_3$, Et_2AlCl were 50, 50, 0.5, and 4 mmoles, respectively. Toluene, 5 mL. Open circles are at 30°C, half-filled circles are at 10°C, and filled circles are at 0°C.

The Reduction Reaction of $FeCl_3$-$Et_{3-n}AlCl_n$ in Acetonitrile

It is to be noted in this catalytic system that diethylaluminum chloride has more effective activity than other aluminum compounds when it is combined with ferric chloride. Diethylaluminum chloride also has better catalytic activity than ethylaluminum dichloride in a homopolymerization of acrylonitrile as shown in Table 4. The polymerization rate, however, decreased markedly after 30 min, although there was a large quantity of monomer remaining. Since the catalytic activity seemed to depend upon the reduction ability of organoaluminum compounds against ferric chloride, the reduction reaction of the catalytic systems was studied in acetonitrile by a polarographic method in order to examine the correlation with the catalytic
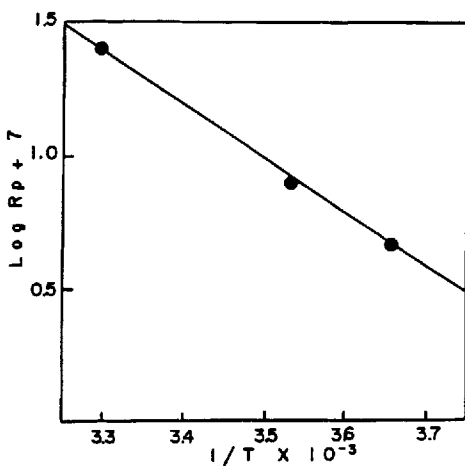
FIG. 6.   Arrhenius plots of overall polymerization. See Fig. 5
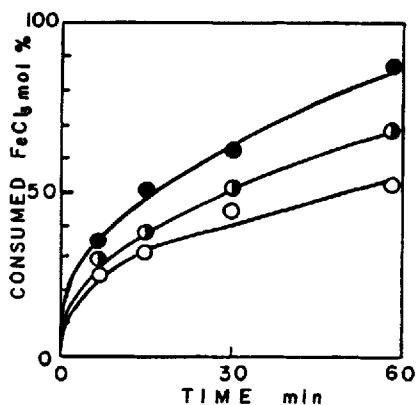legend for conditions.

FIG. 7.   Reduction reaction of $FeCl_3$ with Et_2AlCl. Acetonitrile,
$FeCl_3$, and toluene were 100 and 0.5 mmole and 12 ml, re-
spectively.   Reaction temperature 30°C. Et_2AlCl: (●) 4 mmoles;
(◐) 2 mmoles; (○) 1 mmole.

TABLE 4. Polymerization of Acrylonitrile with $FeCl_3-Et_{3-n}AlCl_n$ [a]

Run No.	Catalyst	mmoles	Yield (g)	Conversion (mole %)	$[\eta]$
19	$Et_3Al/FeCl_3$	4/0.5	Trace		
20	$Et_2AlCl/FeCl_3$	4/0.5	0.461	8.7	0.14
21	$EtAlCl_2/FeCl_3$	4/0.5	0.068	1.3	0.05
22[b]	$Et_2AlCl/FeCl_3$	4/0.5	0.130	2.4	0.72
23[c]	$Et_2AlCl/FeCl_3$	4/0.5	0.534	10.1	0.35
24	$Et_2AlCl/FeCl_2$	4/0.5	0.096	1.8	0.47

[a]Polymerization conditions: Acrylonitrile 100 mmoles, toluene 12 ml, 30°C, 30 min.

[b]The catalyst was reacted for 90 min in 5 ml acetonitrile at 30°C, then the monomer was added to it.

[c]The catalyst was prepared in the presence of the monomer and 5 ml acetonitrile at -78°C.

activity. As shown in Fig. 7, the rate of reduction reaction increases
with the concentration of diethylaluminum chloride, and the concentra-
tion of ferric chloride decreases with time. The rate of reduction of
the ferric chloride by ethylaluminum dichloride was much smaller than
that by diethylaluminum chloride. The relation between reduction re-
actions of these systems and homopolymerization data suggested that
the polymerization reaction was occurring during the reduction re-
action of ferric chloride.

TABLE 5. Reduction Reaction of $FeCl_3$ by $Et_{3-n}AlCl_n$ (n = 1, 2) in
Acetonitrile[a]

	Al/Fe, (mmoles)	Reaction time (min)	Remaining $FeCl_3$ (mole %)
Et_2AlCl	4/0.5	15	50
$EtAlCl_2$	4/0.5	15	96

[a]Conditions: Acetonitrile 100 mmoles, toluene 12 ml, reaction
temperature 30°C.

Electron Paramagnetic Resonance of the Catalytic Systems

It was suggested by the polarographic analysis of ferric chloride,
that the activity of species for the polymerization reaction is closely
related to the valence state of ferric chloride, and electron para-
magnetic resonance examination of the catalytic system in various
conditions was investigated. Ferric chloride has d^5 electrons in the
inner shell, and electron paramagnetic resonance spectra are ob-
served at room temperature. The changes in spectra of the catalytic
systems during the polymerization were examined.

EPR Spectra of $FeCl_3$ in Acetonitrile-Toluene

It is shown in Table 6 that ferric chloride both in acetonitrile-
toluene (vol 1:1) mixture and in a solid state gave a strong Lorenz-
type signal. Golding et al. reported that ferric chloride in acetone
showed a spectrosplitting factor of g = 2.016 with an absorption line
of half width 55 gauss as a single complexed ion $FeCl_4^-$ [7].
Hirano et al. postulated that ferric chloride was a dimer type in
ether solution of 7×10^{-2} mole/l concentration at H_{msl} 600 gauss [8].

It was shown that an absorption line of half width of ferric chloride was 130 gauss in acetonitrile solution at a concentration of 10^{-2} mole/l, so that ferric chloride seemed to be a rather monomeric form coordinated with acetonitrile.

EPR Spectra of Catalytic System in Acetonitrile-Toluene

The changes of EPR spectra of the catalytic system are shown in Fig. 8. The signal of ferric chloride in the system decreased with time at 30°C in acetonitrile, and this change corresponded to the reduction reaction of ferric chloride. After 90 min, a very weak 6-line hyperfine structure appeared in the total length of the spectrum of about 450 gauss. It was due to the interaction of organoaluminum compounds having a 5/2 atomic nucleus spin of aluminum atoms with ferric chloride [9].

TABLE 6. EPR Spectra of $FeCl_3$ in Acetonitrile-Toluene[a]

	$FeCl_3$ (mole/l)	H_{msl} (gauss)	g value
1	3.6×10^{-1}	172	2.02
2	2.9×10^{-2}	128	2.03
3	5.5×10^{-3}	68	2.02
4	5.5×10^{-4}	66	2.03
5[b]		480	2.01

[a]Toluene and acetonitrile (vol 1:1).
[b]$FeCl_3$ in the solid state.

EPR Spectra of Homopolymerization and Copolymerization Systems

EPR spectra of these catalytic systems were also observed in the presence of monomers. Their behaviors were similar to that of the acetonitrile solution of ferric chloride, that is, the stationary 6-line hyperfine structure was observed after 30 min in the acrylonitrile polymerization system. In the case of the butadiene and acrylonitrile copolymerization system, this phenomenon appeared after 10 hr under the same condition. These results are closely connected with the polymerization data; the polymerization reaction proceeds during the period in which the decreasing signal of ferric chloride can be observed. In these polymerization systems, the signal with 6 lines was
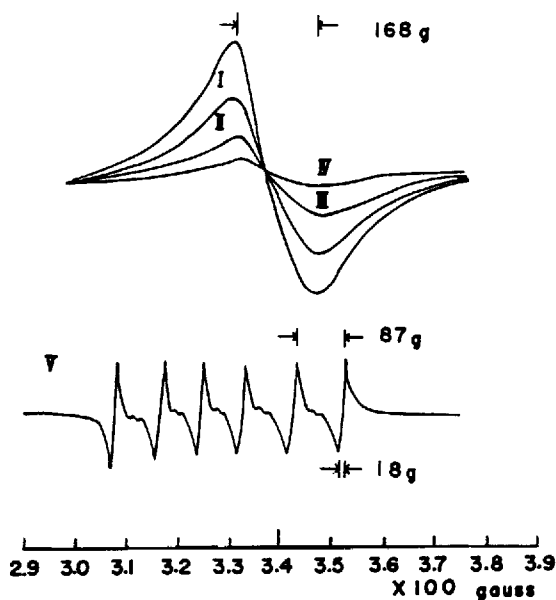
FIG. 8. EPR spectra of $FeCl_3$ with Et_2AlCl in acetonitrile and toluene. Acetonitrile, $FeCl_3$, and Et_2AlCl were 100, 0.5, and 4 mmoles, respectively. Toluene, 12 ml. Measured at 30°C. Reaction times: I: 7 min; II: 15 min; III: 30 min; IV: 60 min; V: 90 min.

superposed on the spectrum of ferric chloride and it seems that the reduction reaction proceeds through complexing with organoaluminum halides and ferric chloride [9].

EPR Spectra of Homopolymerization and Copolymerization by Radical Initiator in the Presence of Diethylaluminum Chloride

As shown in Fig. 9, a EPR signal was also observed in the polymerization system initiated by benzoyl peroxide in the presence of diethylaluminum chloride. Bamford et al. reported that ESR spectra of polymer radicals in the radical polymerization of acrylonitrile were observed as a single line H_{msl} 28 gauss at 90°K [10].
Figure 9-I shows that a single signal having a spectrosplitting factor of 2.01 with an absorption line width of 40 gauss was observed in the free radical polymerization of acrylonitrile in the presence of diethylaluminum chloride. Acrylonitrile was polymerized at 50°C by benzoyl peroxide for 15 min and rapidly frozen to -150°C. In the

case of the copolymerization, the signal g value of 2.06 of broader line-width (100 gauss) was observed as shown in Fig. 9-II. A signal was not observed in the free radical polymerization in the absence of diethyl aluminum chloride by the same method.
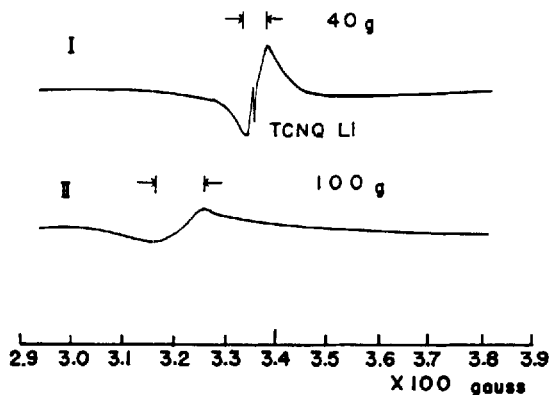

FIG. 9. EPR spectra of radical-initiated polymerization systems in the presence of Et_2AlCl. I: AN, BPO, and Et_2AlCl were 100, 0.5, and 4 mmoles, respectively; toluene, 12 ml. II: AN, BD, BPO, and Et_2AlCl were 50, 50, 0.5, and 4 mmoles, respectively; toluene, 12 ml. Both measured at -150°C.

CONCLUSION

It was concluded that in these catalyst systems, the most effective catalyst is ferric chloride and diethylaluminum chloride.

A polymerization reaction was induced as far as the reduction reaction of ferric chloride took place. The reduction occurred through a complex formation between diethylaluminum chloride and ferric chloride, probably proceeding with alkylation of ferric chloride.

$R.FeCl_2.RAlCl_2$ is very unstable and induced the polymerization reaction. Although the reduction reaction proceeded quantitatively, the efficiency for formation of active species of polymerization was not high. The difference between diethylaluminum chloride and ethylaluminum dichloride in catalytic activity depended mainly upon the reduction reaction; the reduction rate was so small that unreacted ferric chloride retarded the polymerization, though the ethylaluminum dichloride had a much greater ability of activating acrylonitrile monomer by complex formation.

An EPR signal of ferric chloride was not observed in the ferric chloride and triethylaluminum system at 30°C, and it was concluded that for this system the reduction reaction was too fast to form species having catalytic activity.

ACKNOWLEDGMENT

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