Studies in Cyclocopolymerization. XII. Cyclocopolymerization of the Donor:Acceptor Pair 1,4-Diene:Monoolefin Lewis Acid Complex

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ABSTRACT

Acrylonitrile (AN) is known to form a cyclocopolymer with 1,4-dienes such as divinyl ether (DVE) and 3,3-dimethyl-1,4-pentadiene with radical initiators. Since AN has a high tendency toward homopolymerization, the copolymers are not of regular structure. Lewis acids such as $ZnCl_2$ and $Al(Et)_3$ were used in this paper to increase the e-values of AN and methacrylonitrile (MAN) through complexation. AN, MAN, and 2- and 4-vinylpyridine were copolymerized with DVE and 1,4-pentadiene with Lewis acids. In all cases the rate of copolymerization was much enhanced and the alternating tendency of the cyclocopolymer increased with the amount of added Lewis acids. A 1:2 DVE:AN alternating cyclocopolymer was obtained spontaneously or with AIBN with $Al(Et)_3$ in hexane. Also 1:2 alternating cyclocopolymer was successfully obtained in acetone by using a large amount of $ZnCl_2$. The identification of charge-transfer (CT) complex-ation between the DVE and $(AN)_2ZnCl_2$ complex, and between the 1-hexene and $(AN)_2ZnCl_2$ complex may support the par-ticipation of a CT complex formed between all 1,4-dienes studied and the monoolefin-Lewis acid complexes in the

cyclocopolymerization mechanism to increase the rate
and the alternating tendency.

INTRODUCTION

Stable 1:1 and 2:1 complexes of acrylonitrile (AN) [1], meth-
acrylonitrile (MAN) [1] or methyl methacrylate with $ZnCl_2$ are formed
readily by dissolving $ZnCl_2$ in a monomer and distilling off the excess
uncomplexed monomer. The complexes can be precipitated from a
solution of $ZnCl_2$ in a monomer with nonpolar solvents such as alkanes
or diethyl ether. The complexes of AN and MAN with $ZnCl_2$ show
shifts of C≡N stretching absorptions to higher frequencies and C=C
stretching absorptions to slightly lower frequencies indicating a
localization of electron density toward the metal through conjugation.
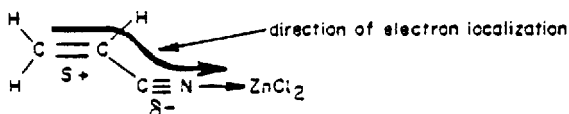
Homopolymerizability and copolymerization behavior of these
olefins which have conjugated nitrile or carbonyl groups change by
addition of Lewis acids such as $ZnCl_2$ into the polymerization system.
Free radical homopolymerizations of AN, MAN, and methyl meth-
acrylate proceeded at a much higher rate when $ZnCl_2$ was used [2].
In copolymerization these monomers behaved as those which had
more positive e-values when polymerized in the presence of
$ZnCl_2$ [3]. It is a general trend that a wider difference in polarity
of the double bonds of comonomers in opposite directions gives
more alternating tendency in copolymerization. The formation of
an alternating copolymer appears to be the result of molecular
complex formation between comonomers such as styrene and
maleic anhydride [4]. When the donor compound is fixed, the charge-
transfer (CT) complexation is stronger when the acceptor has a
larger electron affinity. The electron affinity of acceptors appears
to be parallel to the e-values of acceptors.
In cyclocopolymerization with donor 1,4-dienes, maleic an-
hydride (e = 2.25), and fumaronitrile (e = 1.96) are examples of
powerful acceptor monomers, which form cyclocopolymers of 1:2
(diene:monoolefin) alternating structure [5]. The fact that they do
not homopolymerize under usual polymerization conditions, together
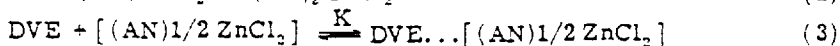with their large positive e-values, leads to the formation of

alternating copolymers. If maleic anhydride and fumaronitrile are the ideal acceptor monomers for a donor 1,4-diene, monomers such as AN ($e = 1.20$) and MAN ($e = 0.40$) are less ideal because they are known to homopolymerize with ease and because their electron affinities are not very high. Alternating copolymers of AN and MAN with styrene ($e = 0.8$) [1, 6] and propylene ($e = -0.78$) [7] were successfully obtained by using Lewis acids. Some authors attributed the formation of alternating copolymers to the CT complexation between a donor monomer and, for example, the AN–Lewis acid complex. The formation of alternating copolymers of AN, MAN, and methyl methacrylate complexed with Lewis acids would be rather surprising if copolymerization were mere random copolymerization of, for example, styrene with the AN (Lewis acid) complex. It is well known that addition of a Lewis acid enhances the homopolymerizability of AN, MAN, and methyl methacrylate to a great extent [2]. It has also been reported that these Lewis acid-base complexes form 1:1 CT complexes with aromatic compounds [1b].

In this paper, cyclocopolymerization of AN, MAN, 2-vinylpyridine (2VP), and 4-vinylpyridine (4VP) with divinyl ether (DVE) and 1,4-pentadiene (PD) was studied using $ZnCl_2$ and $Al(Et)_3$ as Lewis acids. Since there is no suitable solvent which dissolves the $ZnCl_2$ complexes without dissociation, copolymerization of the $ZnCl_2$ complexes was carried out in most cases in bulk, excess AN or MAN serving as solvent.

RESULTS AND DISCUSSION

Charge-Transfer Complex of Donor 1,4-Diene:Acceptor Monoolefin-Lewis Acid Complex Pair

An ultraviolet (UV) spectral study was conducted on the system of DVE and $ZnCl_2$ in AN as the solvent at $24°C$. One can consider two kinds of equilibria in this system: one is the Lewis acid-base complexation of AN with $ZnCl_2$ (Eqs. 1 and 2), and the other is the CT complexation between DVE and the $(AN)_2 ZnCl_2$ complex (Eq. 3):

$$AN + ZnCl_2 \rightleftharpoons (AN)ZnCl_2 \tag{1}$$

$$AN + (AN)ZnCl_2 \rightleftharpoons (AN)_2 ZnCl_2 \tag{2}$$

$$DVE + [(AN)1/2\, ZnCl_2] \overset{K}{\rightleftharpoons} DVE...[(AN)1/2\, ZnCl_2] \tag{3}$$

By using AN as the solvent, one can expect that the equilibrium of the Lewis acid-base complexation is very much shifted toward the

$(AN)_2 ZnCl_2$ side. All the dissolved $ZnCl_2$ was assumed to be in the form of $(AN)_2 ZnCl_2$. The solution of DVE and $ZnCl_2$ in AN showed a tremendous enhancement of absorption compared with the absorptions of the components (Fig. 1). This enhancement was interpreted as due to a contact type of CT complexation between DVE and $(AN)_2 ZnCl_2$ complex. The continuous variation plot
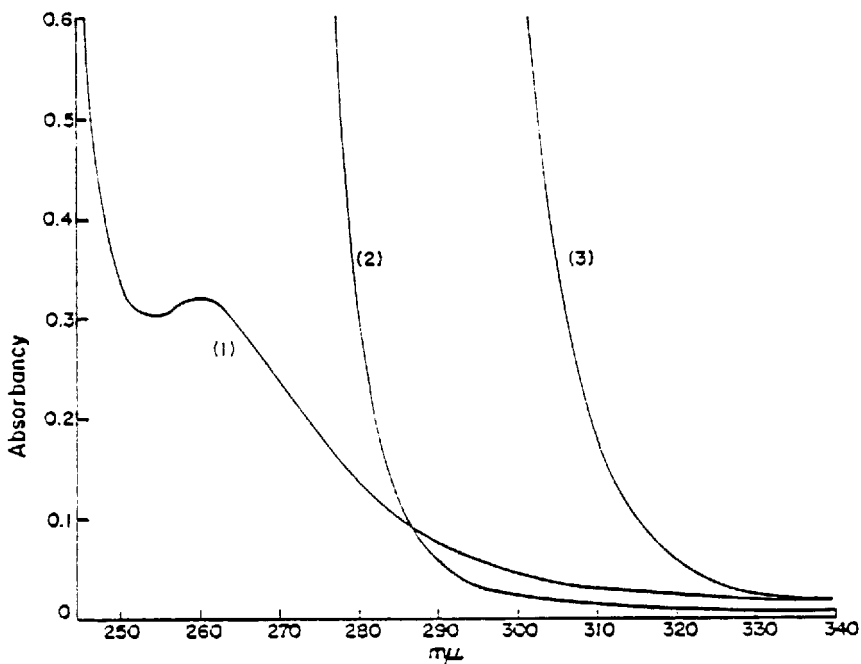
FIG. 1.   UV absorptions of DVE... $[(AN)1/2 ZnCl_2]$ CT complex and its components in AN as solvent at $24°C$.   (1) $2[ZnCl_2] = 1.621$ mole/liter; (2) [DEV] = 1.621 mole/liter: and (3) [DVE] = 1.621 mole/liter, $2[ZnCl_2] = 1.621$ mole/liter.

(Fig. 2) confirmed that this enhancement was due to a complexation of DVE and $(AN)_2 ZnCl_2$ complex because a maximum was observed at the molar ratio of $[DVE]/[(AN)1/2 ZnCl_2] = 1/1$.
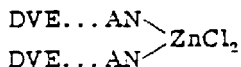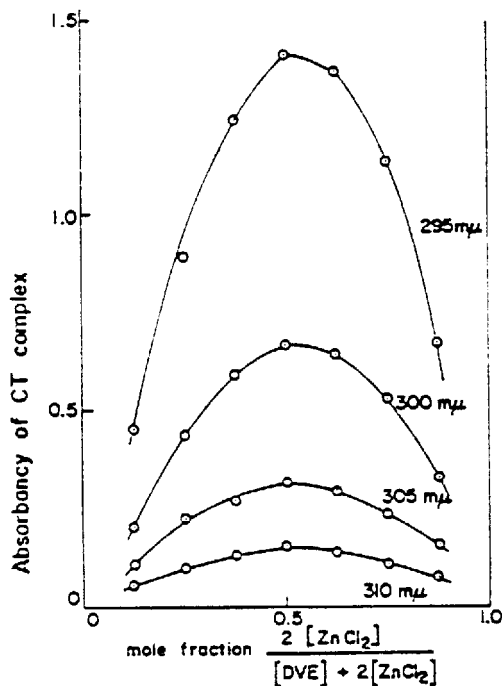
DVE...AN
           $>$ZnCl_2
DVE...AN

FIG. 2. Continuous variation plot of DVE...[(AN)1/2 ZnCl$_2$] CT complex in AN as solvent at 24°C. Total concentration of [DVE] + 2[ZnCl$_2$] = 3.242 mole/liter.

1-Hexene was used as a model compound for 1,4-pentadiene in the study of CT complexation with the AN-ZnCl$_2$ complex in AN as the solvent at 24°C. The UV absorptions of the components are shown in Fig. 3. 1-Hexene, ZnCl$_2$, (AN)$_2$ZnCl$_2$, and AN did not absorb at wavelengths greater than 245 mμ when analyzed separately. But when 1-hexene was added to the solution of (AN)$_2$ZnCl$_2$ in AN, absorption became very strong even at 255 mμ, which shifted bathochromically with the amount of 1-hexene added. Also, in this system a small absorption appeared at 297 mμ. It was considered that both absorptions, the one at 297 mμ and the other starting at 260 mμ, were due to CT complexation between 1-hexene and (AN)$_2$ZnCl$_2$. The smaller absorption at 297 mμ was used to study CT complexation. The continuous variation plot in Fig. 4 shows a maximum absorption at the molar ratio of [hexene]/AN1/2 ZnCl$_2$] = 1/1.
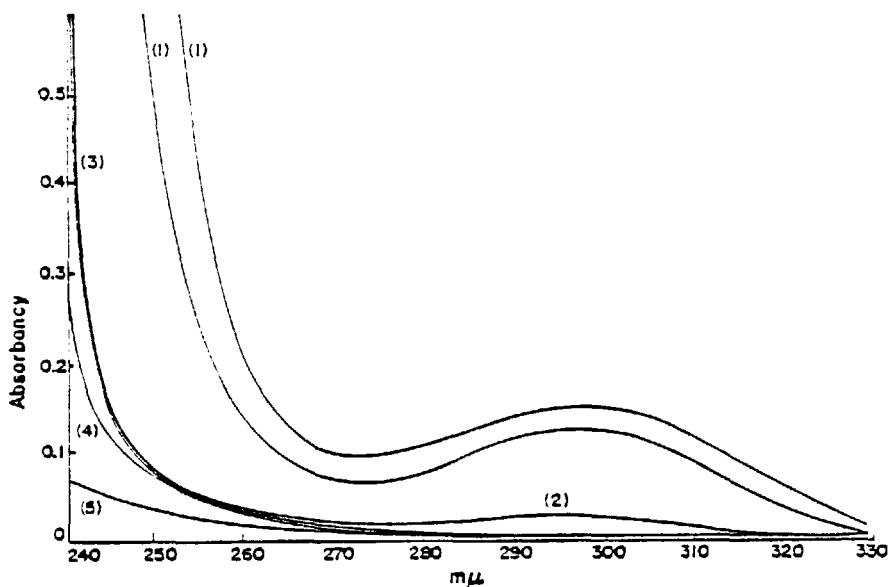
FIG. 3. UV absorptions of hexene...$[(AN)1/2\,ZnCl_2]$ CT complex
and its components. (1) $ZnCl_2$ + AN + hexene vs AN + hexene;
(2) AN + dioxane vs dioxane; (3) hexene + AN vs AN; (4) $ZnCl_2$ +
AN vs AN; and (5) $ZnCl_2$ + dioxane vs dioxane.

This again indicates a 1:1 complexation between a donor (1-hexene)
and AN which is complexed with $ZnCl_2$, since $ZnCl_2$ complexes with
2 moles of AN in AN.

hexene...AN
            $ZnCl_2$
hexene...AN
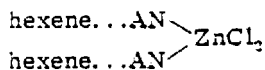
The equilibrium constant of the CT complexation was estimated to be
K ≃ 0.27. The Scott plot is shown in Fig. 5.

The CT complexation between a donor compound and a monoolefin-
Lewis acid complex was interpreted as the result of increased electron
affinity of the monoolefin through complexation with a Lewis acid, be-
cause AN alone did not show any evidence of CT complexation with
either DVE or 1-hexene in n-heptane as the solvent.

In the following sections, cyclocopolymerization studies using
Lewis acids are described. The results were compared with those
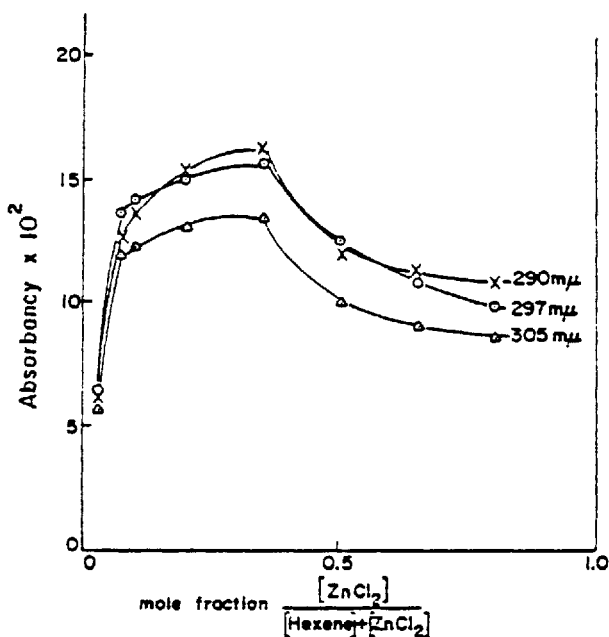
FIG. 4. Continuous variation plot of hexene... $[(AN)1/2\,ZnCl_2]$ CT complexation. $[hexene] + [ZnCl_2] = 1.94$ mole/liter in AN as solvent.
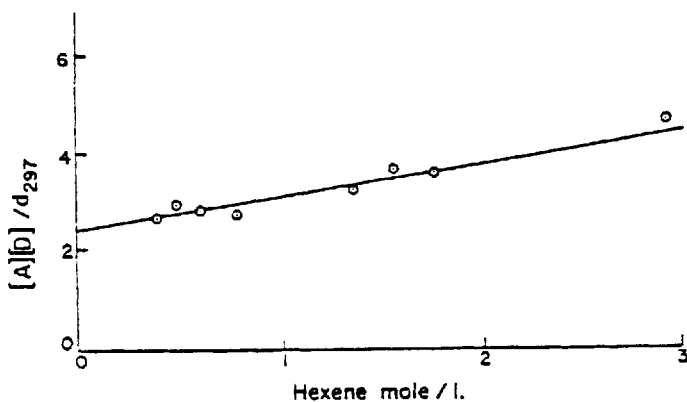
FIG. 5. Scott plot of hexene... $[(AN)1/2\,ZnCl_2]$ CT complex at 297 mμ. $K \simeq 0.27$, $\epsilon \simeq 1.5$, and $[(AN)_2\,ZnCl_2] = 7.61 \times 10^{-2}$ mole/liter.

obtained in the copolymerization without Lewis acids. It was expected that the electronic localization of monoolefins which was brought about by complexation with Lewis acids would lead to a more alternating cyclocopolymerization with donor 1,4-dienes through CT complexation.

Copolymerization of AN with DVE

A copolymer composition study of the AN-DVE copolymer prepared without Lewis acid was reported by Barton, Butler, and Chapin [5a]. If AN and DVE formed a weak CT complex, a photopolymerization of the CT complex would encourage the "homopolymerization" of the dative state of the CT complex, thus forming a more alternating copolymer [8]. However, no evidence of CT complexation of this pair could be found in the UV region in heptane. As shown in Table 1, the results of the photopolymerization through Pyrex glass tubes were the same as with AIBN-initiated copolymerization. Although Pyrex glass cuts off light with a wavelength shorter than 290 mμ, the results may be analogous to polymerization with no CT complexes present and no Lewis acids present.

TABLE 1. Photopolymerization of AN with DVE in Pyrex Glass Bulk, 24°C.

Run No.	Mole fraction of AN in feed	Yield of polymer (wt%)	Mole fraction of AN in copolymer	
			This experiment	With AIBN by Barton et al. [5a]
P-AN-DVE-3	0.30	0.14	0.745	0.70
P-AN-DVE-87	0.87	0.66	0.898	0.89

Copolymerization of AN with DVE was studied by adding ZnCl$_2$ in different concentrations. When DVE was added to 1:1 or 2:1 AN-ZnCl$_2$ pure Lewis acid-base complex, two layers formed. The upper layer consisted mainly of DVE and the lower layer was mainly AN-ZnCl$_2$ complex. Then a vigorous exothermic reaction occurred spontaneously in the lower phase, producing much insoluble rubbery polymer. The elemental analysis of the polymer indicated that the AN fraction in the polymer was 0.42. The complex alone does not polymerize with such ease. ZnCl$_2$ is almost insoluble in DVE. The same vigorous

spontaneous polymerization occurred when ethyl vinyl ether was added to the AN-ZnCl$_2$ complexes.

The mole fraction of AN in the copolymer decreased toward 0.5 and the copolymerization showed more alternating tendency with increasing ZnCl$_2$ concentration. These results are shown in Tables 2, 3, and 4 and Fig. 6. These polymerization reactions were started from homogeneous mixtures. Since dioxane dissolves ZnCl$_2$ slightly, a very dilute solution copolymerization was carried out in dioxane. Though the molar ratio of [ZnCl$_2$]/[AN] was high, the concentration of AN-ZnCl$_2$ complex may not be so high because dioxane may dissociate the complex.

TABLE 2. Bulk Copolymerization of DVE with AN in the Presence of ZnCl$_2$[a]

Run No.	Mole fraction of AN in feed	$[M_1 + M_2]$ in feed (moles $\times 10^{-2}$)	Reaction time (min)	Yield (wt%)	Mole fraction of AN in copolymer
Zn-A-D-3	0.30	12.67	7	1.13	0.668
Zn-A-D-5	0.50	7.60	7	0.81	0.703
Zn-A-D-7	0.70	8.69	10	3.25	0.752
Zn-A-D-9	0.90	8.44	5	0.54	0.833

[a][AIBN] = 2.02 $\times$ 10^{-2} mole/l., [AN]/[ZnCl$_2$] = 20/1, at 50°C.

There were no vinyl absorptions in the IR, indicating complete consumption of both double bonds of the diene. In these experiments the copolymer composition was never exactly 1:2 or 1:1 (= DVE:AN), but there was a strong tendency toward alternating copolymerization with ZnCl$_2$, judging from the copolymer composition curves. It appears that the addition of ZnCl$_2$ facilitated the formation of repeating units (I) and (II) through CT complexation of DVE with the AN-ZnCl$_2$ complex.

Since the AN-ZnCl$_2$ complex did not dissolve in nonpolar solvents, the dilution of the AN-ZnCl$_2$ complex without dissociation was not possible. This difficulty prevented the realization of an alternating cyclocopolymer whose composition would be constant 1:1 or 1:2 because of the high reactivity of the AN-ZnCl$_2$ complex [2] and free AN.

TABLE 3. Copolymerization of IVE with AN in the Presence of $ZnCl_2$ in Dioxane

Run No.	Mole fraction of AN in feed	$[M_1 + M_2]$ (mole/liter)	$[AIBN]$ (mole/liter) $\times 10^{-3}$	Reaction time (min)	Yield (wt%)	Mole fraction of AN in copolymer
D-Zn-A-D-30	0.30	0.757	5.78	190	22	0.564
D-Zn-A-D-45	0.45	0.572	5.51	190	~8b	0.612
D-Zn-A-D-70	0.70	0.408	5.48	190	25	0.698
D-Zn-A-D-85	0.85	0.350	4.76	190	20	0.770

a[AN]/[$ZnCl_2$] = 1.88 at 80°C.
bNot quantitative.

TABLE 4. Spontaneous Copolymerization of DVE with AN in the Presence of $ZnCl_2$[a]

Run No.	Mole fraction of AN in feed	$[M_1 + M_2]$ (moles $\times 10^{-2}$)	Reaction temperature (°C)	Reaction time (min)	Yield (mg)	Mole fraction of AN in copolymer
Bulk/Auto-5	0.50	7.60	60	9	148	0.516
Bulk/Auto-85	0.85	7.61	24	50	45	0.663

aBulk, [AN]/[$ZnCl_2$] = 4.97.
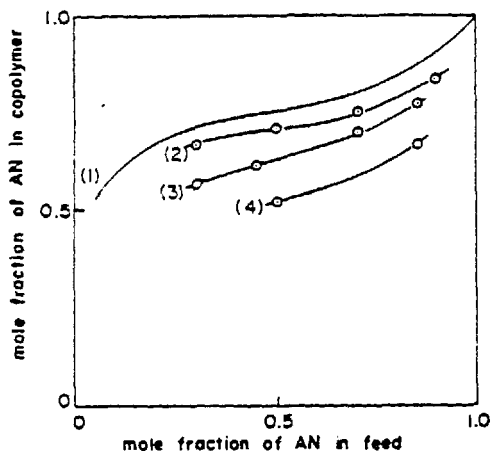
FIG. 6. Copolymerization of DVE with AN with $ZnCl_2$. (1) Without $ZnCl_2$, by Barton, Butler, and Chapin [5a]. (2) Bulk, $AN/ZnCl_2$ = 20, 60°C, with AIBN. (3) In dioxane, $AN/ZnCl_2$ = 1.87, with AIBN. (4) Bulk, $AN/ZnCl_2$ = 4.97, spontaneous polymerization at 60°C and 24°C.
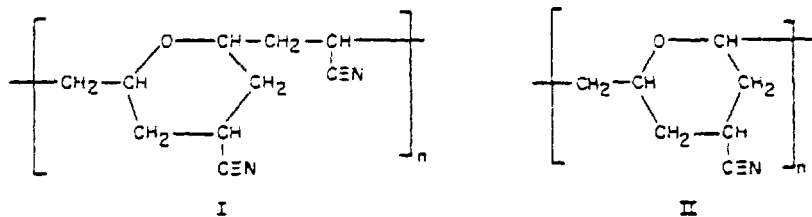
The extremely exothermic spontaneous copolymerization which occurred when DVE was added to the $AN-ZnCl_2$ complex may be evidence of the CT complexation and its initiation through the dative state of the CT complex. Aromatic compounds such as benzene, toluene, and styrene are known to form 1:1 CT complexes with $AN-ZnCl_2$ or $MAN-ZnCl_2$ complexes. Styrene copolymerizes with $AN-ZnCl_2$ or $MAN-ZnCl_2$ spontaneously, producing 1:1 alternating copolymer [1]. The alternating tendency in the present cyclocopolymerization with $ZnCl_2$ may be due to the CT complexation between DVE and the $AN-ZnCl_2$ complex.

It has been known that in copolymerization the monomer reactivity ratios, r_1 and r_2 change little with temperature. That is, the difference

in the activation energies of k_{11} and k_{12} $(= \Delta E_{11} - \Delta E_{12})$ and the
difference in the activation energies of k_{22} and k_{21} $(= \Delta E_{22} - \Delta E_{21})$
are interpreted to be not very great. In the system of DVE-AN with
$ZnCl_2$, we may consider at least four potentially reactive species
to undergo copolymerization: free AN, free DVE, AN-$ZnCl_2$ complex,
and DVE...AN-$ZnCl_2$ CT complex. If a "homopolymerization" [6] of
DVE...AN-$ZnCl_2$ CT complex proceeded simultaneously with some
copolymerization of the individual components, the copolymer
composition might change with temperature in favor of the reaction
having the lowest activation energy, because the "homopolymeriza-
tion" of the DVE...AN-$ZnCl_2$ CT complex is thought to have a differ-
ent activation energy from copolymerization of the individual
components of the system. Since most of the copolymerizations of the
DVE-AN pair with $ZnCl_2$ were carried out at 60 C, a lower temper-
ature polymerization of this system was tried for comparison. The
polymerization was initiated thermally and photochemically. The
results are in Table 5.

TABLE 5. Copolymerization of DVE with AN in the Presence of
$ZnCl_2$ at Low Temperature without Initiator[a]

Run No.	Energy source	Temp (°C)	Reaction time(hr)	Yield (mg)	Mole fraction of AN in copolymer
Th-1	Thermal	24	8.5	51	0.695
Th-2	Thermal	0	12.5	10	0.703
UV-1	UV > 290 mμ	24	0.16	30	0.712
UV-2	UV > 290 mμ	-20	1.3	10	0.692
cf. Copolymer of DVE-AN without $ZnCl_2$					0.77 [5a]

[a]Bulk, AN 2.0 ml, DVE 2.0 ml, [AN]/[$ZnCl_2$] = 7.40. Mole
fraction of AN in feed = 0.579.

Little difference in the copolymer composition was found in these
temperature ranges and no evidence of "homopolymerization" of the
DVE...AN-$ZnCl_2$ CT complex, which may have given a 1:1 regular
structure, was obtained at the lower temperature, although the DVE
content in the copolymer became larger than the DVE-AN copolymer
prepared without $ZnCl_2$. It may be seen that the copolymer
composition of this system is a function of only the $ZnCl_2$ concentration.

That is, the DVE...AN-ZnCl₂ CT complex, if active, undergoes
"copolymerization" with either the AN-ZnCl₂ complex or free AN,
or both.

Copolymerization of AN with DVE in the Presence of ZnCl₂ in Acetone

The role of the Lewis acid-base complex of AN-ZnCl₂ in forming a
CT complex with DVE can be studied in a solvent which dissolves
ZnCl₂, such as acetone. In acetone solution the added small amount
of ZnCl₂ will be dissolved in the solvent and mostly uncomplexed with
AN. The copolymerization of the DVE-AN pair in acetone with and
without a small amount of ZnCl₂ showed no difference in rate of
polymerization. This may be because the concentration of AN-ZnCl₂
complex was very small in acetone and, hence, there was very little
CT complexation between DVE and the AN-ZnCl₂ complex (Eq. 3).
The results are shown in Table 6. The difference in solubility of the
copolymer was interesting: a more acetone-soluble copolymer was
obtained with ZnCl₂.
    However, even in acetone the equilibrium of the Lewis acid-base
complexation, Eqs. (1) and (2), can be shifted toward the AN-ZnCl₂
complex side by using a large amount of ZnCl₂ and the concentration
of the CT complex (Eq. 3) will be larger. Thus an alternating
copolymer would be expected by using a large amount of ZnCl₂ in
acetone. Thus the copolymerization was carried out in acetone by
using a large excess of ZnCl₂. The results are shown in Table 7
and Fig. 7.
    The rate of copolymerization became much faster (cf. the results
in Table 6). Note that the monomer concentration was about 1/4 of
that used in the experiments in Table 6, and almost constant 1:2
(DVE:AN) copolymer composition was realized. Since there were no
vinyl absorptions in the IR spectra of the copolymers, these co-
polymers of 1:2 composition were considered to be alternating
copolymers of structure I.

Copolymerization of MAN with DVE in the Presence of ZnCl₂

Radically initiated bulk copolymerizations at a constant feed of
0.519 mole fraction of MAN with different concentrations of added
ZnCl₂ were carried out. The results in Table 8 show that the DVE
content in the copolymer increased with increasing ZnCl₂, and that
the copolymer composition approached 1:1, indicating an increasing
alternating tendency with more ZnCl₂. Similar to the copolymerization

TABLE 6. Copolymerization of DVE with AN in the Presence of $ZnCl_2$ in Acetone (1)[a]

Mole fraction of AN in feed	AN (ml)	DVE (ml)	Acetone (ml)	Yield (mg)			
				With $ZnCl_2$		Without $ZnCl_2$	
				Acetone soluble	DMF soluble[b]	Acetone sol[b]	DMF sol[b]
0.133	0.2	1.8	5.0	124	-	-	120
0.371	0.6	1.4	5.0	150	Trace	3	192
0.578	1.0	1.0	5.0	198	Trace	12	170
0.746	1.4	0.6	5.0	203	22	28	213
0.925	1.8	0.2	5.0	18	158	159	-
1.000	2.0	-	5.0	-	267		
Autopolymerization at 60°C, reaction time 120 min							
0.578	1.0	1.0	5.0	4	-		

[a][AN]/[ZnCl₂] = 7.40, AIBN 50 mg, at 60°C, 40 minutes.
[b]The copolymer was insoluble in acetone but soluble in DMF.

TABLE 7. Copolymerization of DVE with AN in the Presence of ZnCl$_2$ in Acetone (II)[a]

Mole fraction of AN in feed	AN (ml)	DVE (ml)	Acetone (ml)	ZnCl$_2$ (g)	Reaction time (min)	Yield (mg)[b]	Mole fraction of AN in copolymer
0.264	0.4	1.6	20	9.81	20	105	0.618
0.478	0.8	1.2	20	9.81	50	790	0.642
0.847	2.0	0.5	20	9.81	20	675	0.678

[a]AIBN 60 mg, at 60°C.
[b]Copolymer was soluble in acetone.
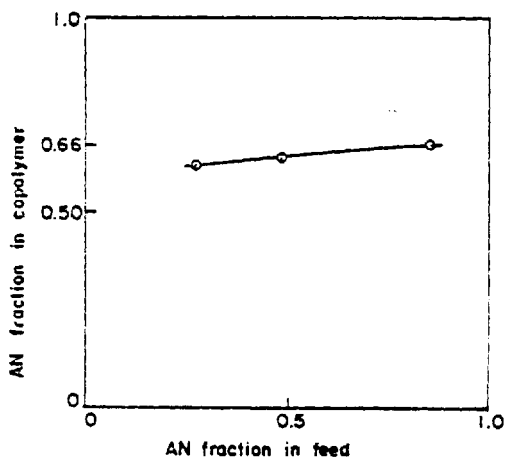
FIG. 7. Copolymerization of DVE with AN in acetone with large amount of ZnCl$_2$ at 60°C.

of DVE-AN with ZnCl$_2$, the results were interpreted as a copolymerization of DVE...[(MAN)1/2 ZnCl$_2$] CT complex with MAN-ZnCl$_2$ complex. An enhancement of rate was observed with ZnCl$_2$ concentration. The acceleration of the rate of polymerization at higher concentration of ZnCl$_2$ may be due to the precipitation of growing radical and lack of termination as the polymerization proceeded in the precipitate. When the concentration of ZnCl$_2$ was 1.306 mole/liter (MAN-DVE-5), a vigorous exothermic autoacceleration occurred.

TABLE 3. Copolymerization of DVE with MAN in the Presence of $ZnCl_2$[a]

Run No.	$ZnCl_2$ (g)	Reaction time (min)	Yield (mg)	Mole fraction of MAN in copolymer
MAN-DVE-0	None	300	160	0.756
MAN-DVE-25	0.183	25	77	
MAN-DVE-20	0.255	15	~37[b]	0.697
MAN-DVE-175	0.243	15	58	.
MAN-DVE-14	0.326	15	85	
MAN-DVE-12	0.378	15	113	
MAN-DVE-10	0.475	15	~84[b]	0.624
MAN-DVE-8	0.592	17	505	0.630
MAN-DVE-5	1.066	15	~ 2 g[c]	0.520

[a]Bulk at 60°C, MAN 3 ml, DVE 3 ml, AIBN 30 mg. Mole fraction of MAN in feed = 0.519.
[b]Not quantitative.
[c]Vigorous exothermic autopolymerization occurred.

Copolymerization of 1,4-Pentadiene with AN in the Presence of $ZnCl_2$

1,4-Pentadiene (PD) was used as the 1,4-diene in place of DVE. Again, a large molar ratio of AN vs $ZnCl_2$ must be used because the nonpolar PD caused precipitation of the AN-$ZnCl_2$ complex and formed two layers when PD was added to the solution of $ZnCl_2$ in AN. The results of the copolymerization of the PD-AN pair in the presence of $ZnCl_2$ are shown in Table 9. Because of the problem of precipitation of the AN-$ZnCl_2$ complex, the copolymerization study was limited to lower PD concentrations in the feed.

A free-radical copolymerization of 3,3-dimethyl-1,4-pentadiene with AN was reported by Butler and Kasat [5b]. It was found that AN predominated in the copolymer. There was little alternating tendency, although cyclization was nearly complete. The mole fraction of AN in the copolymer was 0.956 when that in the feed was 0.857.

Analogous to the copolymerization of DVE-AN in the presence of $ZnCl_2$, two important observations were noted from Table 9:

TABLE 9. Copolymerization of PD with AN with and without ZnCl$_2$[a]

Run No.	Mole fraction of AN in feed	AN (ml)	PD (ml)	Reaction time (min)	With ZnCl$_2$ DMF soluble	With ZnCl$_2$ Insoluble	Without ZnCl$_2$ DMF soluble	Without ZnCl$_2$ Insoluble	Mole fraction of AN in copolymer
A-P-85	0.85	4.25	1.33	60			{131	36	0.894
Zn-AP-85	0.85	4.25	1.33	20	{391	227			0.772
A-P-65	0.65	3.25	3.10	60			27	Trace	
Zn-AP-50	0.50	2.50	4.42	20	{223 / 7	44 (from lower layer) / 0 (from upper layer)			

[a]Bulk at 60°C, with 40 mg of AIBN. When with ZnCl$_2$, [AN]/[ZnCl$_2$] = 6.28.

1) the content of PD increased with ZnCl$_2$ concentration, and 2) the
rate of copolymerization increased with ZnCl$_2$ concentration. These
observations can be explained by a copolymerization of PD...AN-ZnCl$_2$
CT complex with AN-ZnCl$_2$ and/or free AN complex. The identifica-
tion of the 1-hexene...[(AN)1/2 ZnCl$_2$] CT complex may support this
explanation.

The IR spectra of these copolymers showed no vinyl absorptions,
indicating almost complete cyclization. The insoluble product may be
due to accidental cross-linking or chain transfer reactions.

Copolymerization of 1-Hexene with AN in the Presence of ZnCl$_2$

As in the case of the PD-AN-ZnCl$_2$ and the DVE-AN-ZnCl$_2$ sys-
tems, when 1-hexene was added to the solution of ZnCl$_2$ and AN, the
precipitated lower layer, which was mainly AN-ZnCl$_2$ complex with
dissolved hexene in it, polymerized spontaneously producing a
DMF-soluble copolymer. The dative state of the CT complex of
hexene...[(AN)1/2 ZnCl$_2$] was thought to be responsible for the
initiation. The spontaneous polymerization was studied in a
homogeneous system using small amounts of hexene. The results
are shown in Table 10 and Fig. 8.

Copolymerization of DVE with 4-Vinylpyridine and 2-Vinylpyridine in the Presence of ZnCl$_2$

2-Vinylpyridine (2VP) and 4-vinylpyridine (4VP) are known to
form stable complexes with ZnCl$_2$ [9]. It was reported that homo-
polymerization of complexed vinylpyridines proceeded at a higher
rate than uncomplexed vinylpyridines, and that the vinyl group of 2-
methyl-5-vinylpyridine (e = -0.42) became positively polarized by
complexation with ZnCl$_2$ (e changed to +0.81) [9]. Radical co-
polymerization of 4VP with DVE was studied by Butler, Vanhaeren,
and Ramadier [5c]. It was reported that the mole fraction of 4VP
in the copolymer was from 0.348 to 0.999 in the range of 4VP mole
fraction in the feed between 0.15 and 0.85. Copolymerization of 4VP
and 2VP with DVE was studied in the presence of ZnCl$_2$, in order to
compare the results with the copolymerization in the absence of
ZnCl$_2$.

The results are shown in Table 11. When ZnCl$_2$ was used, the
DVE content of the copolymer increased slightly and the rate of
copolymerization of 4VP with DVE in methanol became more than
four times as fast as that without ZnCl$_2$. Since methanol, which dis-
solves ZnCl$_2$ well, was the solvent, complete complexation of vinyl-
pyridines with ZnCl$_2$ could not be expected.

TABLE 10. Spontaneous Copolymerization of 1-Hexene with AN in the Presence of $ZnCl_2$ [a]

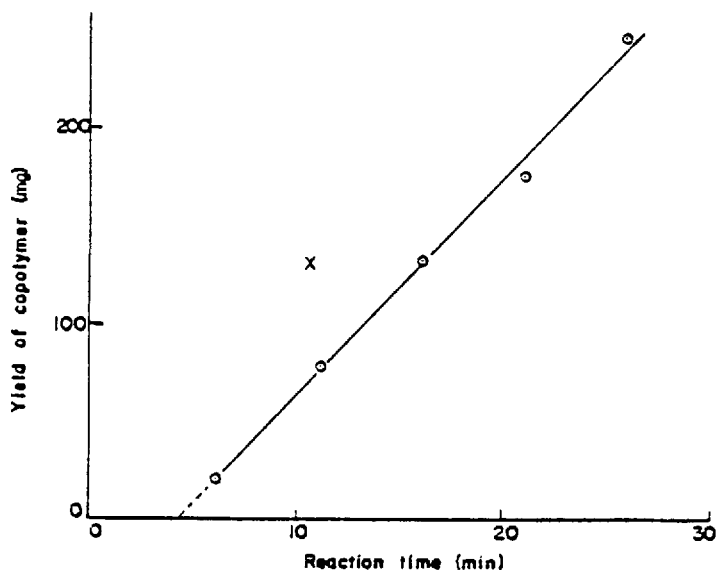| Run No.	Mole fraction of AN in feed	AN (ml)	Hexene (ml)	Reaction temp (°C)	Time (min)	Yield (mg)	Mole fraction of AN in copolymer
AH-908-1	0.908	5.0	1.0	60	6	20	0.875
AH-908-2	0.908	5.0	1.0	60	11	76	
AH-908-3	0.908	5.0	1.0	60	16	131	
AH-908-4	0.908	5.0	1.0	60	21	174	
AH-908-5	0.908	5.0	1.0	60	26	244	0.880
AH-908-0	0.908	5.0	1.0	45	20	48	
AH-952-1	0.952	5.0	0.5	60	11	149	0.927
AH-952-0	0.952	5.0	0.5	45	20	90	

[a] Bulk, $[AN]/[ZnCl_2] = 4.70$.

FIG. 8. Spontaneous copolymerization of 1-hexene with AN with $ZnCl_2$, bulk, $60°C$, $AN/ZnCl_2 = 4.70$. (⊙) Mole fraction of AN in feed = 0.908. (×) Mole fraction of AN in feed = 0.952.

Copolymerization of DVE with AN in the Presence of Al(Et)₃ in Hexane

Copolymerization of DVE with AN was studied using $Al(Et)_3$ as the Lewis acid for AN. Since $Al(Et)_3$ dissolved in the nonpolar solvent, hexane, dilution of the $AN-Al(Et)_3$ complex was possible without much dissociation. When AN was added to a solution of $Al(Et)_3$ in hexane, an intense yellow color developed, indicating Lewis acid-base complexation. AN (0.5 ml) in 20 ml of hexane produced no polymer after 2 days at $25°C$ using an equimolar amount of $Al(Et)_3$. DVE (1.0 ml) in 20 ml of hexane with $Al(Et)_3$ did not polymerize after 2 days at $25°C$. However, when DVE was added to a solution of AN and $Al(Et)_3$ in hexane, a slow spontaneous polymerization occurred at $25°C$. The spontaneous copolymerization was carried out by using equimolar amounts of AN and $Al(Et)_3$ in a nitrogen atmosphere. The results are shown in Table 12 and Fig. 9. The almost constant copolymer compositions and IR spectra of the products indicated that the spontaneous copolymerization produced alternating cyclo-copolymers of 1:2 (DVE:AN) composition (Structure I); the gel

TABLE 11. Copolymerization of DVE with 4VP and 2VP with $ZnCl_2$ in Methanol[a]

Run No.	Mole fraction of VP in feed	$(VP)_2ZnCl_2$ complex (g)	DVE (ml)	Reaction time (hr)	Yield (mg)	Mole fraction of VP in polymer	
						This experiment	Without $ZnCl_2$ [5c]
With $(4VP)_2ZnCl_2$ complex							
425	0.25	0.618	0.972	0.66	45	0.783	0.91
450	0.50	1.235	0.647	0.66	84	0.890	0.98
475	0.75	1.835	0.323	0.66	208	0.895	0.99
With $(2VP)ZnCl_2$ complex							
225	0.25	0.618	0.972	6.0	18	0.792	
250	0.50	1.235	0.647	7.5	67	0.893	
275	0.75	1.853	0.323	29.0	97	0.915	

Without $ZnCl_2$, 4VP-DVE pair

Run No.	Mole fraction of 4VP in feed	4VP (ml)	DVE (ml)	Reaction time (hr)	Yield (mg)
0425	0.25	0.242	0.972	5	27
0450	0.50	0.484	0.647	5	160
0475	0.75	0.727	0.323	3	61

[a] 50 mg of AIBN and 15 ml of methanol were added to each run, at 60°C.

TABLE 12. Copolymerization of DVE with AN with Al(Et)$_3$ in Hexane (I)[a]

Run No.	Mole fraction of AN in feed	AN (ml)	DVE (ml)	Yield (mg)	Mole fraction of AN in feed
Al-3	0.18	0.50	3.00	96	0.622
Al-4	0.30	0.50	1.54	81	0.652
Al-5	0.70	1.00	0.57	57	0.654
Al-6	0.30	1.50	0.50	36	0.694

[a]$[Al(Et)_3]/[AN] = 1/1$. $[AN + DVE] = 1.61$ mole/liter. Spontaneous polymerization at $25°C$ for 26 hr.
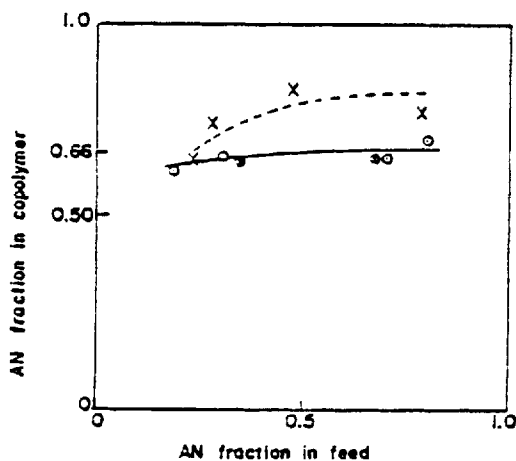
FIG. 9. Copolymerization of DVE with AN with Al(Et)$_3$ in hexane. (⊙) Spontaneous polymerization. $[AN]/[Al(Et)_3] = 1$. (×) With AIBN and catalytic amount of Al(Et)$_3$, at $60°C$. (⊗) With AIBN, at $60°C$, $[AN]/[Al(Et)_3] = 1$.

permeation chromatograph of the products showed only one peak, proving that the polymers were copolymers. The initiation was considered to be caused by the dative state of the CT complex of DVE and the AN-Al(Et)$_3$ complex.

The alternating copolymer could not be obtained when only small amounts of $Al(Et)_3$ were used in the copolymerization: AN composition became larger as shown in Table 13 and Fig. 9. But when equimolar $Al(Et)_3$ and AN were used with AIBN, the same 1:2 alternating cyclo-copolymer, which was soluble in acetone, was obtained at $60°C$. The results are shown in Table 14 and Fig. 9.

The electronic effects in the cyclocopolymerization of 1,4-dienes with monoolefins were also investigated. The success of preparing alternating cyclocopolymers of DVE with AN in acetone by using a large amount of $ZnCl_2$ (Fig. 7) and in hexane by using equimolar amounts of $Al(Et)_3$ and AN (Fig. 9) demonstrated that the greater difference in polarity of the double bonds between a donor and an acceptor, which might lead to a stronger CT complex between them, was essential to obtaining alternating cyclocopolymers.

The cationic initiation of the DVE-AN pair by $(Et)_2O-BF_3$ and the anionic initiation by butyllithium in CH_2Cl_2 produced only homo-polymers of DVE and AN, respectively, judging from the IR spectra of the products. The characteristic absorptions were $C\equiv N$ at $2240\ cm^{-1}$ and the ether group at $1070\ cm^{-1}$. Therefore, initiation of the spontaneous copolymerizations was concluded to be through a radical mechanism.

EXPERIMENTAL

Materials

Reagent grade AN, MAN, 2VP, 4VP, DVE, and 1-hexene were distilled before use. 1,4-Pentadiene was prepared by the method of Benson and McKusick [10]. α,α'-Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. Reagent grade acetone, methanol, hexane, and $ZnCl_2$ were used as received. DVE was pur-chased from Merck, Sharp and Dohme, and $Al(Et)_3$ was purchased from Ethyl Corporation, and used as received.

The complexes of AN and MAN with $ZnCl_2$ were prepared by dis-solving $ZnCl_2$ in an excess of AN and MAN. The complexes were recrystallized from petroleum ether and dried under vacuum [1]. The complexes of 2VP and 4VP with $ZnCl_2$ were prepared in methanol by mixing the components in 2:1 $(VP:ZnCl_2)$ ratio [9c]. The stoichiometry of the complexations was measured by EDTA titration [11] by using eriochrome black as the indicator. The analytical data of 2:1 $VP:ZnCl_2$ complexes used in the copolymeriza-tions were $(4VP)_2ZnCl_2$ complex, % Zn found, 18.8% (theoretical, 18.87%); melting point, found 129-133°C (reported [9c] 124-128°C); $(2VP)_2ZnCl_2$ complex, % Zn found, 18.9% (theoretical, 18.87%); melting point, found, 173-175°C (reported [9c] 118-119°C).

TABLE 13. Copolymerization of DVE with AN with Al(Et)$_3$ in Hexane (II)[a]

Run No.	Mole fraction of AN in feed	Total monomer (moles × 10^{-1})	Total monomer (moles/liter)	[AlEt$_3$] (moles × 10^{-3})	Reaction time (min)	Yield (mg)	Mole fraction of AN in copolymer
Al-AIBN-1	0.222	3.84	1.92	1.46	25	85	0.649
Al-AIBN-3	0.277	3.86	1.93	1.46	25	115	0.733
Al-AIBN-6	0.468	4.11	1.96	1.46	25	104	0.817
Al-AIBN-8	0.782	4.10	2.05	1.46	50	32	0.770

[a] AIBN 50 mg at 60°C.

TABLE 14. Copolymerization of DVE with AN with Al(Et)$_3$ in Hexane (III)[a]

Run No.	Mole fraction of AN in feed	AN (ml)	DVE (ml)	Hexane (ml)	AIBN (ml)	Reaction time (min)	Yield (mg)(wt%)	Mole fraction of AN in copolymer
Al-AIBN-33	0.333	1.00	2.64	20	60	15	432(15.2)	0.647
Al-AIBN-66	0.666	2.00	1.32	20	60	15	193(7.33)	0.647

[a] [AN]/[Al(Et)$_3$] = 1/1, at 60°C.

Spectral Studies

UV spectra were obtained using a Beckman DK-2A spectrophotometer. Quartz cells of 1 cm path length were used. The continuous variation plots were made by using a constant total concentration of $[DVE + 1/2(ZnCl_2)]$, and $[1\text{-hexene} + ZnCl_2]$ for the CT complexes of $(AN)_2ZnCl_2$ with DVE, and 1-hexene, respectively, in AN as the solvent. The absorptions of the complexes were calculated by subtracting the absorptions of pure donors and $(AN)_2ZnCl_2$ numerically. The equilibrium constant of hexene—AN-$ZnCl_2$ CT complex was estimated by using the Scott equation [12] (Eq. 4) which is a rearranged form of the Benesi and Hildebrand equation [13]

$$\frac{[A][D]l}{d} = \frac{1}{K\epsilon} + \frac{1}{\epsilon}[D] \tag{4}$$

where $[A]$ and $[D]$ are concentrations (mole/liter) of the acceptor and the donor, respectively. l is the optical path length (cm), ϵ is the molar extinction coefficient of the complex, K is the equilibrium constant of the complexation, and d is the optical density. Small concentrations of $ZnCl_2$, that is, small concentrations of the $(AN)_2ZnCl_2$ complex, were used.

IR spectra were taken with Beckman IR-10 and IR-8 spectrophotometers. The absorptions of $C=C$ double bonds of DVE at 3070, 1620, 1325, 1200, 1170, 992, and 948 cm^{-1} all disappeared in the cyclocopolymers of DVE. The cyclocopolymers of AN-DVE showed characteristic absorptions of $C\equiv N$ at 2240 cm^{-1} and cyclic ether groups at around 1070 cm^{-1}.

Copolymerization

With ZnCl_2

A solution of $ZnCl_2$ in AN or MAN, donor compound, AIBN, and solvent, when indicated, were put into a Pyrex glass tube which was then sealed under a vacuum of 10^{-5} Torr after repeated freeze-and-thaw cycles with liquid nitrogen. Polymerization was carried out in an oil bath which was thermostatted at $60 \pm 0.02°C$. Complexes of 2VP and 4VP with $ZnCl_2$ (2:1) were prepared and used as the acceptor monomers in the cyclocopolymerization with DVE in methanol. The polymerizations were stopped by opening the glass tubes and immediately pouring the contents into a large amount of 5% aqueous ammonia containing 2 wt% ammonium chloride. The polymer was

reprecipitated from acetone and N.N-dimethyl formamide (DMF) solutions, or washed repeatedly with NH_3-NH_4Cl solution when the polymer was insoluble. The polymer was then washed with a large amount of distilled water and dried under vacuum at 60° C.

With Al(Et)$_3$

A hexane solution of Al(Et)$_3$ was prepared. AN and DVE were added to the hexane solution. Spontaneous copolymerizations were carried out in a dry box under a nitrogen atmosphere. Copolymerization with AIBN was carried out using glass tubes. AIBN, the hexane solution of Al(Et)$_3$, hexane, AN, and DVE were placed in a glass tube, and the tube was sealed on a vacuum line. The polymerization was conducted in an oil bath at $60 = 0.02^\circ$ C. The polymerizations were stopped by pouring the reaction mixture into a hexane-methanol mixture. The polymer was repeatedly precipitated from acetone solution into a large amount of acidic (HCl) 2% aqueous NH_4Cl solution. The polymer was then washed with distilled water and dried under vacuum at 60° C.

Analyses

Copolymer compositions were calculated on the basis of the nitrogen content of the copolymers, which were determined by PCR, Inc., Gainesville, Florida. The number-average molecular weights were measured in acetone by using a Mechrolab Vapor Pressure Osmometer, Model 302. A Gel Permeation Chromatograph of Waters and Associates (Model GPC 300) was used to analyze molecular weight distribution. DMF was used as the solvent and the calibration curve was made by use of monodisperse, standard polystyrene samples which were purchased from Waters and Associates.

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