Donor-Acceptor Complexes in Copolymerization. III. Conjugated Diene-Acrylonitrile Copolymerization in the Presence of Metal Halides

Akio Takahashi[a]; Norman G. Gaylord[a]

[a] Gaylord Associates, Inc., Newark, New Jersey

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AKIO TAKAHASHI and NORMAN G. GAYLORD

Gaylord Associates, Inc.
Newark, New Jersey

SUMMARY

The copolymerization of isoprene or butadiene with acrylonitrile in the presence of zinc chloride or ethylaluminum sesquichloride, in the presence or absence of a free radical catalyst, at 30-70°C yields an equimolar, diene-acrylonitrile alternating copolymer containing more than 90% trans-1,4 unsaturation, irrespective of monomer charge. The copolymer results from the homopolymerization of a diene-acrylonitrile. . .metal halide transoid charge transfer complex. When $ZnCl_2$ is the electron-accepting metal halide and the polymerization is carried out at temperatures of 50°C and higher or to high conversions, the equimolar copolymer is accompanied by a high acrylonitrile polymer, and in the presence of a radical catalyst, by a normal radical copolymer. In the presence of the organoaluminum halide and in the absence of a radical catalyst, the alternating copolymer is the only product, irrespective of monomer charge. However, in the presence of a radical catalyst and at high acrylonitrile monomer charges, e.g., D/AN = 10/90, the alternating copolymer is accompanied by a normal radical copolymer. The formation of equimolar, alternating copolymer at all monomer ratios and in the absence or presence of a radical catalyst indicates that the (D-AN. . .MX) charge transfer complex readily undergoes homopolymerization and does not copolymerize with free diene or acrylonitrile or with the AN-AN. . .MX complex.

INTRODUCTION

The free radical-initiated polymerization of polar monomers such as acrylonitrile and methyl methacrylate, in the presence of metal halides such as zinc chloride and aluminum chloride, is characterized by increased rates of polymerization [1-4]. This effect has been attributed to the formation of a complex between the polar monomer and the metal halide, resulting in delocalization of the electrons in the double bond of the complexed monomer [2-4]. The presence of metal halides also increases the rate and comonomer content in the free radical-initiated copolymerization of olefinic compounds with the complexed polar monomers [5, 6].

The uncatalyzed, spontaneous copolymerization of a-olefins with these polar monomers in the presence of an ethylaluminum halide yields high-molecular-weight, 1:1 alternating copolymers [7, 8].

It has been proposed [1, 9] that the alternating copolymer results from the spontaneous homopolymerization of an equimolar donor-acceptor complex between the olefin and the complexed polar monomer, and that the spontaneous and the free radical-initiated copolymerizations are similar in nature. This proposal was confirmed by (a) the spontaneous copolymerization of styrene and methyl methacrylate in the presence of ethylaluminum sesquichloride [9, 10] and of styrene and acrylonitrile in the presence of zinc chloride [11] to high-molecular-weight, 1:1 alternating copolymers, irrespective of monomer charge, and (b) the increased rate of polymerization in the presence of a free radical catalyst to the same high-molecular-weight, 1:1 alternating copolymer, irrespective of monomer charge [9-11].

The present paper provides further confirmation of the identity of the spontaneous and free radical-initiated copolymerization by the formation of high-molecular-weight, alternating copolymers, independent of monomer ratio, in the copolymerization of acrylonitrile with isoprene or butadiene, in the presence of either zinc chloride or ethylaluminum sesquichloride, both in the absence and in the presence of a free radical catalyst.

EXPERIMENTAL

Materials

Commercial-grade isoprene was distilled over CaH_2. Instrument-grade butadiene was passed through potassium hydroxide and a column of molecular sieves. Research-grade acrylonitrile was distilled. Commercial

zinc chloride (A.C.S. grade) was heated in a vacuum oven at 200-250°C for several hours and handled in a dry box. Ethylaluminum sesquichloride, 25% solution in toluene (Texas Alkyls, Inc.)., was used as received. t-Butyl peroxypivalate (Lupersol 11, Lucidol Division, Pennwalt Corp.), 75% solution in mineral spirits, half life 10 hr at 55°C, was used as received.

Copolymerization

Zinc chloride and solvent, where used, were placed in a three-necked, round-bottomed flask equipped with a Teflon-coated stirring bar, thermometer, reflux condenser, or cold finger and nitrogen outlet and inlet. The flask was flushed with nitrogen and heated to the required temperature while stirring in a nitrogen atmosphere. A solution containing the monomers, a small amount of solvent, and the peroxide, where used, was slowly added through either a dropping funnel or a hypodermic syringe while maintaining the reaction temperature constant. The reaction mixture was stirred for the desired reaction time, in a nitrogen atmosphere at constant temperature.

When ethylaluminum sesquichloride was used as the metal halide, the order of addition was solvent, monomers, peroxide, ethylaluminum sesquichloride. To avoid conventional free radical polymerization when the peroxide was used, the aluminum compound was added immediately following the addition of peroxide.

The reaction was terminated by the addition of methanol containing a small amount of 2,6-di-t-butyl-p-cresol. The methanol-insoluble polymer was filtered, washed with fresh methanol, and dried to constant weight in vacuo at 40-50°C.

In some cases, the methanol filtrate was mixed with benzene, shaken with water containing a small amount of hydrochloric acid in a separatory funnel, washed with fresh water, and the benzene removed in vacuo below 50°C to recover the methanol-soluble polymer. Where further fractionation was desired, the methanol-insoluble polymer was stirred in dimethylformamide, filtered, and washed with a small amount of fresh dimethylformamide to separate the methanol-insoluble polymer into dimethylformamide-soluble and -insoluble fractions. The soluble fraction was precipitated into methanol and the insoluble fraction was washed with methanol and then dried to constant weight.

RESULTS AND DISCUSSION

Copolymerization in the Presence of Zinc Chloride

The copolymerization of isoprene or butadiene with acrylonitrile in the presence of zinc chloride is characterized by the occurrence of one or more of the following reactions:

(1) Absence of free radical catalyst: (a) Spontaneous copolymerization to an equimolar, alternating copolymer. (b) Spontaneous homopolymerization of acrylonitrile.

(2) Presence of free radical catalyst: (a) Spontaneous copolymerization to an equimolar, alternating copolymer. (b) Spontaneous homopolymerization of acrylonitrile. (c) Radical-initiated copolymerization to an equimolar, alternating copolymer. (d) Radical-initiated homopolymerization of acrylonitrile. (e) Radical-initiated, conventional copolymerization to a copolymer whose composition is dependent upon the initial comonomer charge.

These reactions occur concurrently but at different rates. The extent of participation of any individual reaction in a given experiment is a function of the reaction temperature, time, i.e., conversion, $AN/ZnCl_2$ molar ratio, initial monomer charge, and order of addition of reagents (Table 1).

The addition of isoprene to an equimolar mixture of acrylonitrile and $ZnCl_2$ at room temperature results in spontaneous copolymerization to a composition containing 66% acrylonitrile. However, no reaction occurs when the $ZnCl_2/AN$ mole ratio is 0.05 at temperatures below 60°C. The addition of a solution of isoprene and an azo catalyst to an equimolar mixture of acrylonitrile and $ZnCl_2$, at 55°C, after 10 min gives a 30% yield of a polymeric composition containing 85.6% acrylonitrile. However, in the presence of a radical catalyst, an equimolar copolymer is formed at low temperatures, e.g., 30-45°C, or at low conversions, independent of initial monomer charge.

The addition of a monomer mixture or a solution thereof to a suspension of $ZnCl_2$ in a solvent avoids the formation of nonequimolar polymer compositions. However, when the reaction is carried out at higher temperatures, e.g., 60-70°C, and/or to high conversions, the polymer composition is nonequimolar. Thus, the addition of a mixture of butadiene and acrylonitrile (B/AN = 1/9) containing the peroxide catalyst (0.02 mole) to 0.05 mole of $ZnCl_2$ ($ZnCl_2/AN$ = 5/90), at 40°C, after 60 min gave a 144% yield (based on B/AN = 1/1) of a polymer composition containing 68% acrylonitrile.

Similarly, the addition of a mixture of isoprene and acrylonitrile

Table 1. Diene/Acrylonitrile Copolymerization in the Presence of $ZnCl_2$ (MX)

D/AN mole ratio	MX, mole	MX/AN mole ratio	Solvent[a], ml	Catalyst[b], mole	Temp/time, °C/min	Copolymer Yield[c], %	AN, mole %	$[\eta]$[d], dl/g
Isoprene								
50/50	0.2	1/1	B, 50	A, 0.002	55/10	30.3	85.6	
50/50	0.2	1/1	H, 50	T, 0.007	70/90	77.3	56.7	
50/50	0.2	1/1	B, 50	T, 0.007	60/90	56.3	57.7	
9/91	0.06	1/10	0	T, 0.0012	50/10	74.0	57.0	
9/91	0.03	1/20	0	T, 0.0012	45/7	9.6	51.5	
70/30	0.015	1/20	0	T, 0.0012	40/10	5.9	49.3	1.4
Butadiene								
10/90	0.05	5/90	0	T, 0.002	40/60	144.0	68.0	
10/90	0.05	5/90	0	T, 0.002	30/20	21.0	53.0	

[a] B = benzene, H = heptane
[b] A = azobisisobutyronitrile, T = t-butyl peroxypivalate.
[c] Based on 1:1 D/AN.
[d] $CHCl_3$, 25°C.

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Table 2. Isoprene/Acrylonitrile Copolymerization in the Presence of Metal Halide (MX)

I/AN mole ratio	MX, mole	MX/AN mole ratio	Solvent[a], ml	TBPP[b], mole	Temp/time, °C/min	Copolymer		$[\eta]$[d], dl/g
						Yield[c], %	AN, mole %	
Et$_{1.5}$AlCl$_{1.5}$								
9/91	0.006	1/100	0	0	40/50	17.2	53.0	1.7
70/30	0.0189	1/10	0	0	40/3	13.2	46.6	
50/50	0.02	1/10	T, 20	0	40/3	4.7	48.6	
ZnCl$_2$								
9/91	0.03	1/20	0	0	60/60	0	—	
9/91	0.03	1/20	0	0.0012	45/7	9.6	51.5	

[a]T = toluene.
[b]TBPP = t-butyl peroxypivalate.
[c]Based on 1:1 I/AN.
[d]CHCl$_3$, 25°C.

(I/AN = 1) containing 0.007 mole of peroxide catalyst to a suspension of 0.2 mole of $ZnCl_2$ ($ZnCl_2$/AN = 1) in 50 ml of heptane, after 90 min at 70°C gave a 3.9% yield of a methanol-soluble product containing 28.5% acrylonitrile and a 77.3% yield of methanol-insoluble product containing 56.7% acrylonitrile. The latter product was stirred at room temperature in dimethylformamide and was fractionated into 8% of a soluble product containing 90.9% acrylonitrile, and 92% of an insoluble product containing 52.8% acrylonitrile. The unfractionated, nonequimolar compositions are apparently mixtures containing the equimolar copolymer as the predominant component. The latter are soluble in dimethylformamide at room temperature when prepared at $ZnCl_2$/AN ratios of 0.5 or less.

Copolymerization in the Presence of Ethylaluminum Sesquichloride

The copolymerization of isoprene or butadiene with acrylonitrile in the presence of ethylaluminum sesquichloride is characterized by the following reactions:

(1) Absence of free radical catalyst: (a) Spontaneous copolymerization to an equimolar, alternating copolymer.

(2) Presence of free radical catalyst: (a) Spontaneous copolymerization to an equimolar, alternating copolymer. (b) Radical-initiated copolymerization to an equimolar, alternating copolymer. (c) Radical-initiated, conventional copolymerization to a copolymer whose composition is dependent upon the initial monomer charge.

In the absence of a radical catalyst, an equimolar, alternating copolymer is obtained at all monomer ratios, even when Al/AN mole ratio is as low as 0.01. In fact, the alternating copolymer precipitates out as soon as the ethylaluminum sesquichloride is added to the comonomer mixture at room temperature. Considerable amounts of alternating copolymer are formed within a few minutes, particularly when the diene/acrylonitrile mole ratio is close to equimolar and the Al/AN mole ratio is 0.1 or higher. However, irrespective of monomer charge or metal halide content, the product is an essentially equimolar, alternating copolymer (Tables 2 and 3).

In the presence of a free radical catalyst, the comonomer yield is considerably increased without changing the alternating structure of the copolymer. However, when the reaction is carried out at very high acrylonitrile and low metal halide contents, e.g., B/AN/MX = 10/90/1, the alternating copolymer is accompanied by a radical-initiated high acrylonitrile copolymer (Table 3).

Table 3. Butadiene/Acrylonitrile Copolymerization in the Presence of Metal Halide (MX)

B/AN mole ratio	MX mole	MX/AN mole ratio	Solvent[a], ml	TBPP[b], mole	Temp/time, °C/min	Copolymer	
						Yield[c], %	AN mole %
Et$_{1.5}$AlCl$_{1.5}$							
10/90	0.01	1/90	0	0	30/90	3.7	51.6
10/90	0.01	1/90	0	0.002	40/45	14.8	56.7
50/50	0.01	1/20	T, 20	0	40/45	1.4	50.1
50/50	0.01	1/20	T, 20	0.001	40/45	12.2	46.7
ZnCl$_2$							
50/50	0.01	1/20	0	0	40/90	0	–
50/50	0.01	1/20	0	0.001	40/90	1.2	58.7
10/90	0.05	5/90	0	0.002	35/30	13.0	52.5

[a]T = toluene.
[b]TBPP = t-butyl peroxypivalate.
[c]Based on 1:1 B/AN.

General Characteristics of Complex Polymerization

The complexation of a polar monomer such as acrylonitrile with a metal halide increases its electron-accepting ability and enhances the formation of a charge transfer complex with a strong electron donor such as a conjugated diene. The complex is capable of polymerizing spontaneously to an equimolar, alternating copolymer. When the concentration of metal halide is low, the concentration of complex is also low. Depending upon the activating ability, i.e., the electron-accepting strength, of the metal halide, a free radical activator may be necessary to initiate polymerization of the complex. Thus, copolymerization of an equimolar mixture of butadiene and acrylonitrile in the presence of 5 mole-% $ZnCl_2$ requires a radical initiator,
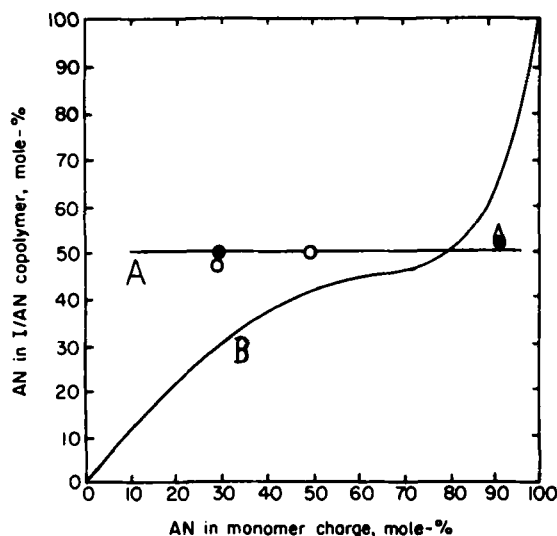
Fig. 1. Copolymerization of isoprene and acrylonitrile. (A) Metal halide-complexed system; (B) conventional free radical system. (●) $ZnCl_2$ + TBPP; (○) $Et_{1.5}AlCl_{1.5}$; (△) $Et_{1.5}AlCl_{1.5}$ + TBPP.

while spontaneous copolymerization occurs under the same conditions in the presence of the same amount of ethylaluminum sesquichloride. However, the use of a free radical initiator in the latter case increases the yield of alternating copolymer about five times.

The formation of alternating copolymer irrespective of monomer charge

(Figs 1 and 2) indicates that the complex does not copolymerize with a monomer, i.e., the growing chain arising from the complex homopolymerization does not add monomer molecules, whether the latter are strong electron acceptors or strong electron donors. Thus, even at low metal halide concentrations, when the complex concentration is low and the free monomer concentration is high, free monomer does not copolymerize with the complex. The formation of high yields of copolymer at low concentrations of metal halide indicates that the metal halide is made available to complex with free acceptor monomer and generate additional charge transfer complex when a charge transfer complex is incorporated into a propagating chain. Since the growing chain does not add free monomer, the maximum conversion is dependent upon the monomer which is present in the lowest concentration.

In the presence of a free radical catalyst, under conditions where the latter is effective in initiating conventional radical copolymerization, radical
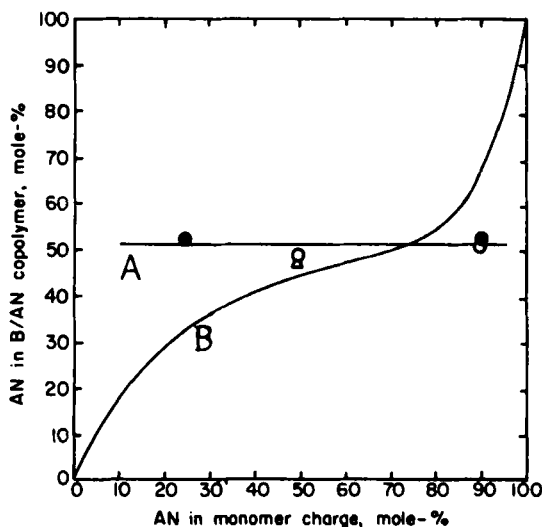

Fig. 2. Copolymerization of butadiene and acrylonitrile. (A) Metal halide-complexed system; (B) conventional free radical system. (●) $ZnCl_2$ + TBPP; (○) $Et_{1.5}AlCl_{1.5}$; (△) $Et_{1.5}AlCl_{1.5}$ + TBPP.

copolymers are formed. However, the rate of the radical copolymerization is significantly lower than that of the complex homopolymerization. Consequently, the radical copolymerization only influences the composition of

the mixture of polymeric products at higher conversions and polymerization temperatures. This is also dependent upon the metal halide concentration, since the latter determines the complex and free monomer concentrations.

Although acrylonitrile that is activated by complexation with a halide preferentially forms a donor-acceptor complex with an electron donor monomer, it also complexes with free acrylonitrile at low concentrations of donor monomer or high concentrations of metal halide. The existence of the 2:1 acrylonitrile-$ZnCl_2$ [12] and the 2:1 methyl methacrylate-$ZnCl_2$ [13] complexes has been confirmed and is considered responsible for the increased rate of homopolymerization of these monomers in the presence of metal halides [1].

It was earlier proposed [1, 9] that the nonequimolar products obtained in the copolymerization of olefins [5, 6, 11] with metal halide-activated polar monomers are copolymers resulting from the copolymerization of the (olefin-polar monomer. . .$ZnCl_2$) complex and the (polar monomer-polar monomer. . .$ZnCl_2$) complex. However, fractionation of the nonequimolar compositions into equimolar copolymers, representing better than 90% of the total product, and residues having a very high polar monomer content, and the appearance of the nonequimolar composition only at high temperatures, high conversions, or high metal halide concentrations, indicates that the (donor monomer-AN. . .$ZnCl_2$) complex is formed preferentially when the donor monomer is present and that the rate of homopolymerization of the (D-AN. . .$ZnCl_2$) complex is greater than the rate of homopolymerization of the (AN-AN. . .$ZnCl_2$) complex or the rate of copolymerization of the two complexes. The preferential formation of the (D-AN. . .$ZnCl_2$) complex is in accordance with the observation [14] that the addition of benzene to a 2:1 acrylonitrile-$ZnCl_2$ complex or a 2:1 methyl methacrylate-$ZnCl_2$ complex results in the separation of equimolar benzene-acrylonitrile-$ZnCl_2$ and benzene-methyl methacrylate-$ZnCl_2$ layers, respectively.

The absence of high polar monomer content in the polymers obtained from systems containing ethylaluminum sesquichloride, in the absence of a free radical catalyst and at other than 10/90 diene/AN charges, as well as in the spontaneous and free radical-initiated copolymerization of styrene and methyl methacrylate [9, 10], indicates either that a (AN-AN. . .Al) or (MMA-MMA. . .Al) complex is not formed or is not stable at temperatures of 25-60°C.

Structure of the Equimolar Copolymer

The structure of the equimolar copolymer was investigated using infrared (IR) and nuclear magnetic resonance (NMR) analyses. The infrared spectra should give information about the microstructure of the diene units in the copolymer, while the NMR spectra is concerned with the diene structure and the relative placement of the diene and acrylonitrile units in the co-polymer. Copolymers containing the diene and acrylonitrile in a 1:1 molar ratio were prepared with a free radical catalyst, with metal halide alone (zinc chloride or ethylaluminum sesquichloride), and with free radical plus the metal halides. The three copolymers prepared with different catalysts but with the same monomer composition were analyzed by IR and NMR, and the results were compared.

The infrared spectra showed no substantial differences in the micro-structure of the diene part among the copolymers, irrespective of the method of preparation. The butadiene-acrylonitrile copolymer contained more than 90% of trans-1,4 units and the remaining 10% were shared by 1,2-vinyl and cis-1,4 units. A slightly higher 1,2-vinyl content was found in the free radical-initiated copolymer as compared to the copolymers obtained from the metal halide-complexed systems.

Similarly, no significant differences were observed in the infrared spectra of the isoprene-acrylonitrile copolymers obtained from the three different catalytic systems. It is very difficult to analyze the microstructure of the diene units from the infrared spectra of isoprene-acrylonitrile copolymers with a 1:1 molar composition, since the bands assigned to the isoprene unit either disappear or become very weak and broad. In fact, only one weak and broad band at 850 cm^{-1}, which is assigned to the 1,4-structure of the isoprene unit in polyisoprene, was observed. Since both cis- and trans-1,4 units appear at 850 cm^{-1}, it is difficult to determine each structure independently. However, it is reasonable to assume that the isoprene units are essentially all trans-1,4 since the copolymers with 1:1 molar composition from the free radical and the complex systems gave the same IR spectra, and the diene units in the butadiene-acrylonitrile copolymers were found to have more than 90% of trans-1,4 structure.

The NMR spectra of the copolymers were recorded from CDCl$_3$ solutions at a resonance frequency of 100 Mc/sec at room temperature and are discussed in detail elsewhere [15]. The spectra of all of the isoprene-acrylonitrile copolymers contained peaks at 7.71 and 7.78 τ, assigned to the methylene proton of an isoprene-acrylonitrile diad, while the spectra of all of the butadiene-acrylonitrile copolymers contained a peak at 7.70 τ, assigned to the methylene proton of a butadiene-acrylonitrile diad.
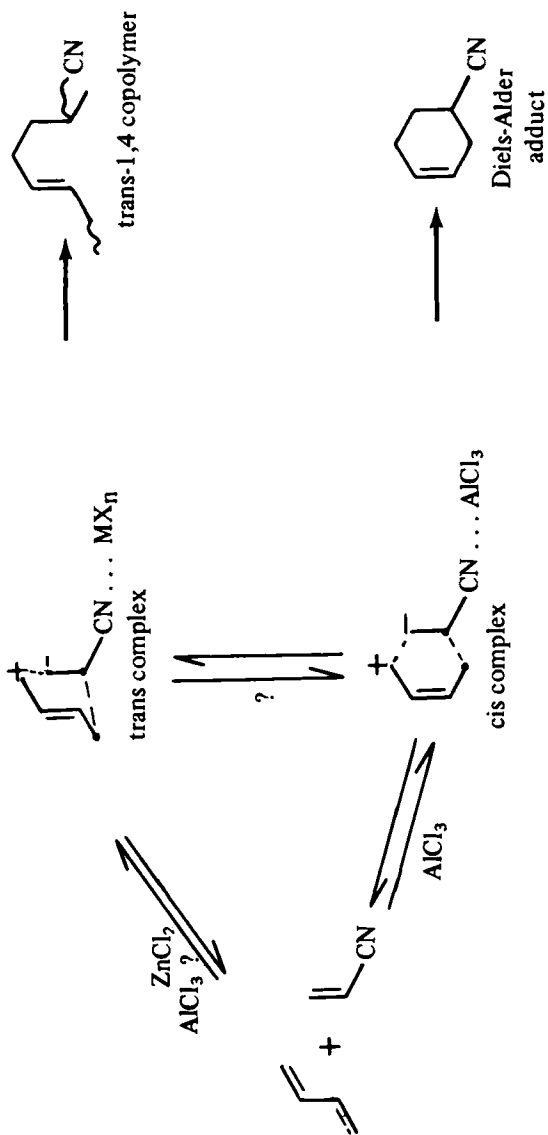
In addition, the spectra of the radical-initiated copolymers contained a peak which was absent in the spectra of the copolymers prepared in a metal halide-complexed system either in the presence or absence of a radical catalyst. A peak at 7.92 τ in the spectrum of the isoprene-acrylonitrile copolymer and a peak at 7.87 τ in the spectrum of the butadiene-acrylonitrile copolymer are assigned to isoprene-isoprene and butadiene-butadiene diads, respectively.

The equimolar copolymers prepared in the presence of a metal halide in the absence or presence of a free radical catalyst, irrespective of diene-acrylonitrile monomer charge, are apparently alternating copolymers containing more than 90% trans-1,4 unsaturation.

The diene monomers are known to exist in the transoid structure at room temperature. Thus, butadiene contains 93-97% of trans-1,4 structure [16], while isoprene contains more than 80% of trans-1,4 structure [17-19]. Since the transoid structure of the diene is dominant in both the monomer and the copolymer with acrylonitrile, it is reasonable to assume that no stereoregulated polymerization took place in the complexed system, i.e., the diene was copolymerized with acrylonitrile maintaining its own stereostructure. Therefore, the diene probably formed a trans-type of charge transfer complex, as shown on the preceding page.

It is generally acknowledged that in the diene synthesis the Diels-Alder adduct forms via a cis type of charge transfer complex between the diene and the dienophile. Although the cis type is energetically more stable than the trans type, the formation of the cisoid or the transoid complex may depend upon the electron-accepting tendency of the dienophile, i.e., a strong electron acceptor may reduce the distance between the donor and acceptor molecules and change the structure of the diene from trans to cis by forming a cisoid complex, whereas a weak acceptor results in a transoid complex. The AN. . .ZnCl$_2$ complex must be a weak acceptor as compared with the AN. . .AlCl$_3$ complex, since aluminum trichloride is a far stronger electron-accepting metal halide than zinc chloride, and thus the Diels-Alder adduct was obtained only when AlCl$_3$ was used as catalyst [20].

Thus, the charge transfer complex of diene and zinc chloride-complexed acrylonitrile is assumed to be an energetically unstable transoid type, a transitory contact type of charge transfer complex [21]. The unstable contact charge transfer complex apparently undergoes polymerization readily, resulting in the formation of an alternating diene-acrylonitrile copolymer with a high transoid diene structure, whereas the more stable cisoid complex results in the formation of the Diels-Alder adduct [20].

REFERENCES

[1] N. G. Gaylord and A. Takahashi, *J. Polymer Sci.*, **B6**, 743 (1968).

[2] M. Imoto, T. Otsu, and Y. Harada, *Makromol. Chem.*, **65**, 180 (1963).

[3] M. Imoto, T. Otsu, and M. Nakabayashi, *Makromol. Chem.*, **65**, 194 (1963).

[4] M. Imoto, T. Otsu, and S. Shimizu, *Makromol. Chem.*, **65**, 174 (1963).

[5] M. Imoto, T. Otsu, B. Yamada, and A. Shimizu, *Makromol. Chem.*, **82**, 277 (1965).

[6] G. E. Serniuk and R. M. Thomas (to Esso Research and Engineering Co.), U.S. Pat. 3,183,217 (May 11, 1965); U.S. Pat. 3,278,503 (October 11, 1966).

[7] M. Hirooka, H. Yabuuchi, S. Morita, S. Kawasumi, and K. Nakaguchi, *J. Polymer Sci.*, **B5**, 47 (1967).

[8] M. Hirooka, H. Yabuuchi, J. Iseki, and Y. Nakai, *J. Polymer Sci.*, **A-1**, **6**, 1381 (1968).

[9] N. G. Gaylord and A. Takahashi, *J. Polymer Sci.*, **B6**, 749 (1968).

[10] N. G. Gaylord and H. Antropiusova, *J. Polymer Sci.*, **B7**, 145 (1969).

[11] N. G. Gaylord and H. Antropiusova, *Macromolecules*, **2**, 442 (1969).

[12] H. Sumitomo, K. Kobayashi, and Y. Hachiyama, *Kogyo Kagaku Zasshi*, **67**, 1652 (1964).

[13] S. Okuzawa, H. Hirai, and S. Makishima, *J. Polymer Sci.*, **A-1**, **7**, 1039 (1969).

[14] T. Ikegami and H. Hirai, *Chem. Commun.*, **1969**, 159.

[15] B. Patnaik, A. Takahashi, and N. G. Gaylord, *J. Macromol. Sci.*, **A4**, 143 (1970).

[16] W. M. Saltman, in *Encyclopedia of Polymer Science and Technology* (H. Mark, N. G. Gaylord, and N. M. Bikales, eds.), Vol. 2, Wiley (Interscience), New York, 1965, p. 678.

[17] M. I. Batuev, A. S. Onischenko, A. D. Nateeva, and N. I. Aronova, *Dokl. Akad. Nauk SSSR*, **132**, 581 (1960); *Chem. Abstr.*, **54**, 22006 (1960).

[18] D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, **83**, 2885 (1961).

[19] J. Gresser, A. Rajbenbach, and M. Szwarc, *J. Am. Chem. Soc.*, **82**, 5820 (1960).

[20] T. Inukai and M. Kasai, *J. Org. Chem.*, **30**, 3567 (1965).

[21] C. N. R. Rao, *Ultraviolet and Visible Spectroscopy*, Butterworth, London, 1961 p. 111.