Alternating Copolymer as New Rubber*

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Summary: As new synthetic rubbers, two types of alternating copolymers are investigated. The alternating copolymer of butadiene and acrylonitrile is prepared by so-called charge-transfer complex in which an alkylaluminum compound as a chelating agent for acrylonitrile and a vanadium compound as a promotor for regeneration of the aluminum compound are employed. A simple use of the aluminum compound requires almost an equimolar amount of the chelating agent against the polymer, but further addition of a catalytic amount of the vanadium compound enables it to produce fifty times the amount of polymer as that of the aluminum compound. The polymer is of the complete regular alternating structure of polyacrylonitrile and *trans*-1,4-polybutadiene capable of crystallizing on stretching. It exhibits high oil resistance as well as excellent tensile strength elongation, rebound elasticity and dynamic elasticity as compared with the conventional nitrile rubber of 50% acrylonitrile. From the kinetic study a step-growth mechanism of the alternating copolymerization is proposed which involves polymerization between the aluminum complexed radical and the complexed monomer consisting of acrylonitrile, butadiene and aluminum compound.

Another type of copolymer is obtained from butadiene and propylene with vanadium and alkylaluminum compound as a catalyst prepared under special conditions, i.e., prepared at -78°C and with use of vanadyl chloride and vanadyl alkoxide in a suitable ratio. In this way the polymer of high alternating structure is obtained in high yield irrespective of the feed monomer ratio. The polymer is a rubber-like mass in spite of its *trans*-1,4 structure of the butadiene unit.

1 Introduction

Alternating copolymerization has been studied for many years and it has been well known that an electron-acceptor monomer such as maleic anhydride and vinylidene cyanide is capable of copolymerizing alternately with an electron-donor monomer like styrene or α -olefin. Acrylonitrile or acrylic ester, on the other hand, is rather too weak as the acceptor to undergo alternating copolymerization but it is found to be activated by Lewis acid like aluminum halide, zinc halide and alkylaluminum dichloride. Hirooka¹⁾ succeeded in preparing an alternating copolymer of acrylonitrile or methylmethacrylate with styrene or propylene by the complexation of the former monomer with ethylaluminum dichloride prior to copolymerization. However, the complexation method requires almost an equimolar amount of complexing agent with respect to the monomer. This fact makes the procedure troublesome and expensive.

Alternating copolymers have not attracted the attention of the plastics industry, perhaps, because

they seem to have lower melting points than those of the homopolymers and do not have better properties than the conventional random copolymers. On the other hand, the lowering of the melting point may be regarded as advantageous to a synthetic rubber, but the alternating copolymer of diolefin has not been known, until Gaylord²⁾ and we³⁾ independently have succeeded in the copolymerization of butadiene and acrylonitrile. Gaylord employed zinc chloride or ethylaluminum dichloride as a complexing agent, whereas we used ethylaluminum chloride together with a transition metal compound like vanadyl chloride, the latter reagent being found to be a useful cocatalyst capable of regenerating the aluminum catalyst. Moreover, the vanadium compound is effective in preventing the polymer from gel-formation. In this way we succeeded in the alternating copolymerization of the diene with acrylic compounds using a catalytic amount of the complexing agent. The alternating copolymer thus obtained is so highly regular that it is crystallizable on stretching. It exhibits high tensile properties and it seems to be promising as a new synthetic rubber.

Another type of alternating copolymer of interest is butadiene-propylene copolymer, which we are

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attempting to develop as an all purpose rubber. Natta⁴⁾ has reported the formation of a small amount of alternating copolymer of butadiene and ethylene as a by-product of the homopolymer. We have succeeded in the preparation of a rubbery propylene-butadiene alternating copolymer in good yield by use of a catalyst composed of organo-aluminum compound and a transition metal prepared under special conditions⁵⁾.

This paper deals with the above two kinds of alternating copolymers as new rubbers with particular emphasis given on the interesting polymerization mechanism.

2 Butadiene Acrylonitrile Copolymer

The alternating polymerization process includes a feature for catalyst preparation, viz it is necessary that a catalytic amount of alkylaluminum halide is complexed with an equimolar amount of acrylonitrile prior to the addition of a vanadium compound, which in a catalytic amount, less than 5% of aluminum compound, acts as a cocatalyst. The direct mixing of aluminum and vanadium components forms merely a simple Ziegler-type catalyst and yields homopolymers of both monomers. The catalyst thus prepared is active even below room temperature and polymerizes a large amount of monomers to give practically completely alternating copolymer of high molecular weight without homopolymers or Diels-Alder addition products. In this reaction the vanadium component is rather considered as a cocatalyst unlike in the Ziegler catalyst, since the aluminum compound itself catalyzes alternating copolymerization but almost an equimolar amount of aluminum compound to the monomer is required. Moreover, the polymer prepared without a vanadium compound is a highly cross-linked and, sometimes, a powdery mass. The vanadium compound is found to be a useful cocatalyst not only to promote the regeneration of the aluminum compound but also to prevent the polymer from cross-linking.

In Table 1 a series of aluminum compounds complexed with acrylonitrile as catalyst is listed. In the catalyst system of aluminum compound—VO(O-Bu)₃(50 : 1), ethylaluminum sesqui- or di-chloride is best, and triethylaluminum and aluminum trichloride are sparingly active, but triethylaluminum becomes active when an equimolar amount of a vanadium halide is employed, perhaps, because triethylaluminum is reacted with the vanadium halide to convert it into ethyl-

Table 1 Effects of aluminum Compounds on the Copolymerization of Butadiene with Acrylonitrile in Toluene at 0°C

Aluminum Compound	Catalytic Activity ($\times 10^{-2}$)	$[\eta]$ (dl/g)
none	0	—
AlEt ₃ ·AN* ¹	0* ⁴	—
AlEt ₂ Cl·AN* ¹	12* ²	—
Al ₂ Et ₃ Cl ₃ ·AN	67	2.06
Al ₂ Et ₃ Br ₃ ·AN	88	1.64
Al ₂ (iBu) ₃ Br ₃ ·AN	17	—
AlEtCl ₂ ·AN	95	1.43
AlCl ₃ ·Et ₂ O	trace* ³	—

Al/VO (t-BuO)₃ = 50/1; Al/total monomer = $1.7 \times 10^{-2}/1$ (g-atom/mol).

*¹ Solvent : (ClCH₂)₂. Al/V = 20/1

*² Grease.

*³ Rubbery solid estimated to be 1 : 1 copolymer from its IR spectrum.

*⁴ Polymer could be obtained after 2-3 days.

aluminum dichloride.

Several kinds of transition metal compounds have been investigated as the cocatalyst. Vanadium, titanium and chromium compounds are found to be best. Table 2 summarizes the results indicating the pronounced effects of cocatalyst on the catalyst activity and on the prevention of the polymer from gel formation. Prior to the addition of cocatalyst to the aluminum compound, the latter must be complexed with acrylonitrile or should be added directly at temperature as low as -78°C.

Solvents play an important role in this sort of polymerization. As is summarized in Table 3,

Table 2 Effects of Vanadium and Titanium Compounds on the Copolymerization of Butadiene with Acrylonitrile in Toluene at 0°C

BD/AN (mol/mol)	V or Ti Compound	Catalytic Activity ($\times 10^{-2}$)	$[\eta]$ (dl/g)	Gel (%)
2	none	2	—	ca. 90
2	VO(Ot-Bu) ₃	95	0.83	8
2	VO(OEt) ₃	60	—	—
2	VO(acac) ₂	68	1.56	ca. 0
2	V(acac) ₃	63	1.58	5
2	VO(Ot-Bu) ₂ Cl	102	1.09	30
2	VO(Ot-Bu)Cl ₂	77	1.31	5
2	VOCl ₃	60	1.40	ca. 0
2	VCl ₄	43	—	—
1	VO(OAc) ₂	22	—	—
1	VO-naph.	43	—	—
2	VCl ₃	38	—	—
2	V ₂ O ₃	28	—	—
2	Ti(O-nBu) ₄	32	1.48	65
2	TiO(acac) ₂	28	—	—
2	TiCl ₄	22	1.62	38
1	Ti-oxalate	28	—	—
1	TiH ₂	28	—	—

Al/V or Ti = 50/1; Al/total monomer = $1.7-2.0 \times 10^{-2}/1$ (g-atom/mol).

Table 3 Copolymerization of Butadiene with Acrylonitrile by the AlEt_3 -AN/ $\text{VO}(\text{Ot-Bu})_3$ System in Various Solvents^{a)}

Solvent	Catalytic Activity ($\times 10^{-2}$)	Gel (%)	η_{sp}/c (dl/g)	$\bar{c}$ (g/dl)
<i>n</i> -Hexane	125	55	0.74	0.335
Toluene	112	36	0.91	0.480
Monochlorobenzene	100	—	—	—
<i>o</i> -Dichlorobenzene	108	—	—	—
Dichloroethane	78	—	—	—
Tetrachloroethylene	153	67	1.08	0.250
Carbon Tetrachloride	132	—	—	—
Diethyl Ether	10	—	—	—
Tetrahydrofuran	0	—	—	—
Acetonitrile	0	—	—	—

a) Polymerization conditions: BD/AN (in feed) = 1/1 (mol/mol), solvent/total monomer = 1/1 (vol/vol), Al/total monomer = $2.5 \times 10^{-2}/1$ (g-atom/mol), Al/V = 20/1 (g-atom/a-atom), mixing order = solvent-AN-BD- AlEtCl_2 -AN- $\text{VO}(\text{Ot-Bu})_3$ (at -78°C), polymerization = $0^\circ\text{C} \times 24$ hr

b) Al/V = 50/1 (g-atom/g-atom), others are same as in the note a).

hydrocarbon solvents are available, but they cause precipitation of the polymer because of its high oil-resistant property. In this connection, halogenated hydrocarbons are suitable. An excess amount of acrylonitrile can be used as solvent capable of dissolving the polymer formed. On the contrary, polar solvents such as ether, tetrahydrofuran, and acetonitrile inhibit the polymerization even in small amounts.

A simple Lewis acid such as aluminum chloride, stannic chloride or zinc chloride itself can be used as the catalyst together with peroxide as proposed by Hirooka and Gaylord. However, for these systems almost an equimolar amount of Lewis acid to the polymer formed is necessary, and moreover the formation of a large amount of gel polymer will take place. Table 4 indicates that the addition of a vanadium compound is also useful

for the above catalyst system to enhance the catalyst efficiency and to prevent the polymer from gel formation.

A more detailed study has been made on the mechanism of the polymerization, and a step-growth mechanism is proposed, since the degree of polymerization increases in the course of polymerization as illustrated in Fig. 1. There seems to be no significant termination but there seems to be a chain transfer reaction to a considerable degree, because there occurs retardation of the polymer growth. In fact, the ratio of polymer yield to the degree of polymerization (Y/P_n) has been found to increase linearly with the extent of reaction, or the polymer yield, except at the final stage of polymerization as shown in Fig. 2. This means that the polymerization involves rapid initiation followed by chain transfer occurring proportionally to the chain growth. In this way the concentration of the active species for initiation and the rates of growth and transfer

Nos. 1, 2, 3 and 4 imply the cases, where $[\text{VOCl}_3]$ are 2.50, 4.00, 7.99 and 20.0 millimole/l, respectively.

Fig. 1 The Increasing Degree of Polymerization of the Polymer with Conversion

Table 4

Lewis' Acid	mmol	BPO mmol	Vanadium Compound	mmol	Polymer (%)	$[\eta]$	AN Content in Copolymer (%)
AlCl_3	1	0.1			14.2	—	50
AlCl_3	1	0.5			14.4	—	49
AlCl_3	1	0.5	VOCl_3	0.05	16.7	0.59	49
AlCl_3	1	0.5	COCl_2	1.00	6.6	0.70	49
SnCl_4	1	0.5			32.8	—	45
SnCl_4	1	0.5	VOCl_3	0.2	17.4	0.58	49
SnCl_4	1	0.5	VOCl_3	1.0	17.8	0.54	50
SnCl_4	1	0.5	$\text{VO}(\text{OEt})_3$	0.5	7.0	0.22	47
SnCl_4	1	0.5	$\text{V}(\text{acac})_3$	0.5	9.7	0.16	47
ZnCl_2	1	0.5			17.4	0.92	40
ZnCl_2	1	0.5	VOCl_3	1.0	10.0	0.54	50
ZnCl_2	12.5	0.5	VOCl_2	1.0	14.5	0.41	47

BD: 25 mmol, AN: 25 mm, Solvent: CH_2Cl_2 2 ml, Polymerization: 25°C , 16 hr.

Fig. 2 Estimated Number of Polymer Chain as a Function of Conversion with Variation of Vanadium Concentration at Constant Aluminum Concentration

	E _i	E _p	E _t	E _{tr}
Radical	20 (Peroxide)	4 (AN)		
Anionic	10 (Redox)	9.3 (BD)	0~2	8~10
Cationic	0	—	—	—
This	1.1 (H _i)	6~8	—	—
		12.3	—	16

are evaluated from the data obtained at varied temperatures. Table 5 lists the activation energies for individual reactions in comparison with the conventional radical and ionic polymerization. It is obvious that the activation energies of the alternating copolymerization are closer to the ionic reaction rather than the radical reaction.

$$[\text{Active species}] = K_i [\text{Al}]^{1/2} [\text{V}]^{1/2} \quad (1)$$

$$R_p \propto [V]^{1/2}[Al]^{3/2} \quad (2)$$

$$R_p = k_p \{K_i[\text{V}]^{1/2}[\text{Al}]^{1/2}\} \{K[\text{BD}][\text{AN}]^n[\text{Al}]\} \quad (3)$$

In conclusion, the polymerization involves the reaction of the complexed growing radical with the monomer complexed with the aluminum compound, as follows

The complex formation of acrylonitrile and ethylaluminum dichloride has been confirmed, and the additional complexation of butadiene is also assumed¹¹.

The resulting BD-AN-Al complex exists in two forms: a stable complex and an excited one (Fig. 3), the latter of which may be responsible for polymerization. The above concept leads to the suggestion that irradiation may be effective to the formation of the excited monomer complex. In fact, the UV-irradiation has been found to enhance the polymerization rate of butadiene—acrylonitrile—Lewis acid system as summarized in Table 6.

Irradiation during the whole stage of polymerization is effective, but partial irradiation in the early stage does not induce post polymerization in the dark, and this fact together with the living nature of the polymerization suggests that the effect of irradiation exists not in the initi-

Fig. 3 The Formation of Charge Transfer Complexes

ation but in the propagation through the excitation of the complexed monomer.

3 Properties of the Alternating Copolymer

The characterization of the alternating copolymer is carried out by IR, NMR and elemental analyses. IR spectrum of the alternating copolymer is almost the same as the conventional one containing 48% acrylonitrile with the exception that the former contains no *cis*-1,4 linkage and only a smaller amount, or a trace, of vinyl linkage. From the result of IR analysis, the alternating copolymer gives the indication only of *trans*-1,4 linkage (970 cm^{-1}) and nitrile group ($2,240 \text{ cm}^{-1}$). According to Morero's method its structure is 98% *trans*-1,4, 2% vinyl and 0% *cis*-1,4.

NMR spectrum of the alternating copolymer gives a characteristic methylene peak of butadiene, as illustrated in Fig. 4. Unlike the conventional copolymer having BD-BD diad (7.87τ) and that of BD-AN (7.72τ), the alternating copolymer possesses only 7.72τ BD-AN diad and the regular alternating structure. In fact, the vulcanizate of the alternating copolymer indicates a discrete crystalline X-ray diagram on stretching in contrast to the amorphous one of the conventional copolymer. As shown in Fig. 5 the alternating copolymer of high molecular weight, whose intrinsic viscosity is 6.5 dl/g , is also crystallizable, and in fact it shows a so-called necking phenomenon on gradual stretching. X-Ray photographs indicate an identity period of $7.27 \text{ \AA}$, which coincides with that of *trans*-1,4 BD-AN alternating unit. The glass temperature is determined by differential scanning calorimetry, and it is found to be -15°C . In other words, it is 5 to 10°C lower than that of the conventional copolymer containing 48% acrylonitrile. Pyrolysis at 500°C shows that the acrylonitrile monomer evolved is much smaller than the conventional copolymer, and this fact is due to the lack of AN-block sequence

Table 6 Effect of Irradiation on Alternate Copolymerization in the Presence of Aluminum Halide at Room Temperature
(BD, 53.2 mmol; AN, 304 mmol; AlCl_3 , 2.1 mmol)

No.	Irradiation	Polym'n. Time (hr)	Convsn.* (%)	Conv./Time (%/hr)	Gel (%)	[AN] in Polymer (mol %)
1	dark	28.15	trace	trace	—	—
2	[UV-Irrad. for 25 min in Early Stage]	720	trace	trace	—	—
3	[UV-Irrad. in the Whole Stage]	0.5	3.8	7.6	2	50.7

* Based on 1 : 1 monomer.

Fig. 4 NMR Chart of Random and Alternating Copolymer

(A): Raw polymer of the alternate at 400% elongation.
(B): Cured rubber of the alternate at 220% elongation.
(C): Cured rubber of the random at 190% elongation.
Fig. 5 Scattered X-Ray Intensity Along Equator Line

which may afford AN-monomer by zipper-like decomposition.

The vulcanizate of the alternating copolymer has been investigated in detail from the industrial point of view. Table 7 summarizes the characteristic behavior of the copolymer in comparison with the conventional random copolymer vulcanized for 60 and 90 minutes at 140°C. Hardness H_s (JIS, Japan industrial standard) and modulus at 200% elongation M_{200} are extremely low as compared with those of the random copolymer, while the tensile strength at break T_s and the ultimate elongation E_B are markedly high. These behaviors have been found to be preserved even at high temperatures. The oil resistant properties are the same in both polymers but the mechanical property of the alternating copolymer under swelling is more superior to that of the random one. Fig. 6 illustrates the stress-strain relationship. In the raw rubbers, alternating

Table 7 Properties of the Cured Rubber

	Alternate		Random (AN : 48%)	
Cure Time (145°C) (min)	60	90	60	90
Original State				
H_s (JIS)	73	74	86	85
M_{100} (kg/cm ²)	43	43	105	114
T_s (kg/cm ²)	237	243	194	205
E_B (%)	400	400	210	200
Hot State (110°C)				
T_s (kg/cm ²)	58		50	
E_B (%)	340		210	
Oil Resistance (Oil: JIS'B',* R.T. × 48 hr)				
Swell (%)	112	112	112	112
T_s (kg/cm ²)	147	153	97	112
E_B (%)	300	290	150	160

* Isooctane/toluene = 70/30.

A: Raw polymer of alternating BD-AN copolymer of a η_{sp}/C of 6.5 at 30°C in 0.5% solution of dimethyl formamide.
B: Raw Polymer of the random reference.
C: Cured rubber of the alternating sample.
D: Cured rubber of the random Reference.

Fig. 6 Stress-Strain Property

copolymer (A) exhibits a considerable strength at high extension, while random copolymer (B) causes a simple plastic flow. The vulcanizate of alternating copolymer (C) is rather low in modulus but high in tensile strength and elongation at break. These phenomena are accounted for by crystallization on stretching. The rebound elasticity of the alternating copolymer shown in Fig. 7 is higher than that of the random one when compared at elevated temperatures. This behavior may be due to the flexible molecular chain, because the alternating copolymer has no interaction between the neighboring AN-units. This idea is confirmed by the stress-optical measurements and ultimate elongation. As illustrated in Fig. 8 the segment length $Z \times l$, where Z and l are the number and the length of the monomer unit in the segment, respectively,

is extremely low as compared with that of the random with the same AN-content. Fig. 9 gives a linear relationship between the ultimate elongation $\lambda_{\max}$ and the function of molecular weight of the cross-linked chain M_c , that of the original molecule M and the unit number in segment Z . Numbers 1, 2, 3 and 4 indicate BD-AN random copolymers whose AN contents are 27.4, 35.6, 42.7 and 48.3%, respectively, and No. 5 indicates the BD-AN alternating copolymer. It has been found that the ultimate elongation of the alternating copolymer is very large as compared with that of the random one and is almost the same as that of BD-homopolymer of *cis-trans* random structure (No. 6). The flexible chain nature of the alternating copolymer is also recognized in the dynamic measurement. As illustrated in Fig. 10 the mechanical loss, $\tan \delta$, is

Fig. 7 Rebound Elasticity

l : Length of unit.
 Z : Ratio of segment length to unit one.

Fig. 8 Stiffness of acrylonitrile-Butadiene Copolymers

Fig. 9 Relation between $\lambda_{\max}$ and $(M_c/MZ)^{1/2}$ of Acrylonitrile-Butadiene Copolymers Fig. 10 Dynamic Moduli E' and E'' and Dynamic Loss $\tan \delta$

rather smaller in alternating copolymer (A) than in random copolymer (B), although the dynamic moduli E' and E'' are lower in the former than in the latter.

4 The Alternating Copolymer of Butadiene and Propylene

Research on alternating copolymer of butadiene and propylene has been attempted, since this type of copolymer has a structure resembling polyisoprene, although the resulting copolymer possesses *trans*-1,4 structure in contrast to the *cis*-1,4 structure of natural rubber. The alternating copolymer of butadiene and ethylene has been reported by Natta⁴⁾, but the resulting polymer is a low molecular weight copolymer with very poor yield. The copolymerization of butadiene and propylene with Ziegler-type catalyst has been reported in literature⁶⁾, but only block copolymer has been obtained. We⁵⁾ have found that the combination of vanadyl chloride and triethylaluminum is a suitable catalyst for alter-

nating copolymerization of butadiene and propylene when the catalyst is prepared at -78°C , unlike the conventional Ziegler-type catalyst prepared at room temperature which yields a simple homopolymer or block copolymer. However, the molecular weight of the alternating copolymer was not sufficiently high, and the product obtained in the early stage of study was rather waxy accompanied by homo-*trans* polybutadiene.

Combination of two types of vanadium compounds, halides and alkoxides, together with triisobutylaluminum was successful in preparing a rubbery product in good yield⁷⁾. Fig. 11 illustrates the yields of low and high polymers as a function of the fraction of vanadyl chloride in the vanadyl chloride and vanadium alkoxide mixed catalyst. In this way, the polymer having an intrinsic viscosity of more than 0.5 dl/g has been obtained in high yield.

Fig. 11 Formation of High (A) and Low Polymer (B) as a Function of Catalyst Composition

The copolymers are found to be of the alternating structure independent of the molecular weight. NMR study indicates that the copolymers possess a methyl proton at 9.15τ and methine one at 4.7τ , whose ratio is 3 : 2, and butadiene-propylene diad at 8.05τ , but no butadiene-butadiene sequence at 7.9τ . In low copolymers besides the above absorption, the peaks arising from vinylidene group have been observed at 8.3τ and 5.3τ . IR analysis also leads to the same conclusion, i.e., methyl and *trans*-1,4 units are observed at 2950 cm^{-1} and 970 cm^{-1} , respectively, and the vinylidene group at 1640 cm^{-1} ($>\text{C}=\text{CH}_2$) and 890 cm^{-1} ($-\text{CH}=-$) in the low polymer. The fact that the low polymer possesses

a terminal vinylidene group may suggest a chain transfer by hydride shift occurring at the propylene terminal unit of the growing chain.

Another evidence for the alternating copolymerization has been found in the facts that (1) the polymers always possess 1 : 1 composition irrespective of the monomer feed composition (Table 8) and (2) the fractionation of the polymer with methanol and benzene gives the fractions of different molecular weights having the same 1 : 1 composition.

Table 8

PP/BD	Yield (%)	Polymer Composition	
		BD	PP
0.6	22	54	46
1.0	31	52	48
2.0	22	52	48
4.0	14	48	52

Catalyst : VOCl_3 0.001, AlEt_3 0.003, toluene 25 cc, prepared at -78°C .

Monomer : BD 0.075 mol and 0.050 mol.

Polymerization : 48 hrs, -30°C .

The alternating copolymer is a rubberlike mass having a glass point of -72°C inspite of its *trans*-1,4 structure with respect to the butadiene unit. The investigation of vulcanized polymer is under examination. Alternating copolymerization can be effected also between butadiene and butene-1 or pentene-1.

5 Conclusion

We have succeeded in the preparation of two types of alternating copolymers which may be considered as new synthetic rubbers, i.e., diolefin-acrylic compound and diolefin- α -olefin. The former is synthesized by alternating copolymerization through the donor-acceptor charge transfer complex, whereas the latter through a different mechanism such as alternating coordination of two monomers to the catalyst. The formation of the charge transfer complex may occur between the two monomers, one being that of low ionization potential (I_p) capable of donating an electron and the other that of high electron affinity (E_A) capable of accepting an electron. In I_p-E_A map (Fig. 12) the monomer locating within the triangle formed by the straight lines, i.e., $I_p + E_A = \text{const}$, and E_A -axis and I_p -axis, might be favorable for the complex formation. Accordingly, the combination among butadiene, isoprene or α -olefin and sulfur dioxide, maleic anhydride, vinylidene cyanide is useful, and acrylic com-

MAH: Maleic acid anhydride.
 MAN: Methacrylonitrile.
 CP: Chloroprene.
 IP: Isoprene.
 VC: Vinyl chloride.
 E: Ethylene.
 IB: Isobutene.
 VDCN: Vinylidene cyanide.
 AN-Al: Aluminum chelated acrylonitrile.
 BD: Butadiene.
 ST: Styrene.
 VDC: Vinylidene chloride.
 PP: Propylene.

Fig. 12 $I_P - E_A$ Map and Charge-Transfer Complex Formation

pounds are also available when they are complexed with a Lewis acid. On the other hand, the com-

bination of α -olefin or vinyl compound with diolefin may be located out of the available region and it becomes effective only through a different route like the alternating coordination. Results of further studies in this field may be published elsewhere.

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