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I. M. Panayotov[a]; G. Heublein[b]
[a] Central Laboratory for Polymers Bulgarian Academy of Sciences, Sofia, Bulgaria [b] Sektion Chemie Friedrich-Schiller Universität Jena, Jena, GDR

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Cationic Polymerization in the Presence of π-Electron Acceptors

I. M. PANAYOTOV

Central Laboratory for Polymers
Bulgarian Academy of Sciences
Sofia 1113, Bulgaria

and

G. HEUBLEIN

Sektion Chemie
Friedrich-Schiller Universität Jena
Jena 69, GDR

ABSTRACT

The cationic polymerization of various vinyl and cyclic monomers was studied in the presence of strong electron acceptors (EA) such as tetracyanoethylene, chloranil, and syn-trinitrobenzene, added in quantities commensurate with the initiator concentrations. In all cases studied, the presence of EA brings about an increase both in the overall polymerization rate and in the molecular weights of the polymers obtained without changing the kinetic scheme of the reaction. The EA added also affects the monomer reactivities in the copolymerization reaction, the insertion of less reactive monomer being favored. The effect of EA was explained in terms of complexation with the counterion which causes a shift of the ionic equilibrium in the system.

The chain carrier in the cationic polymerization can be represented as an electrophilic reaction center (carbenium ion, oxonium ion, etc.) associated with a counterion, . . . -P^+X^-. Chain growth becomes possible when the interaction of the electrophilic center with the monomer which represents a π-donor (polymerization of vinyl monomers) or an n-donor (ring-opening polymerization of heterocyclic compounds) is stronger than with the counterion. It could be expected that strong π-electron acceptors, due to their electrophilic nature, can compete with the active centers of the propagating chain in their interaction with monomers or counterions, thus affecting the chain propagation. Indeed, the investigations, carried out in our laboratories have shown that strong π-electron acceptors (EA) such as tetracyanoethylene (TCE), chloranil (CA), or 1,3,5-trinitrobenzene (TNB) have a definite effect on the course of the cationic polymerization and on the polymers obtained. In the present article some typical results obtained in our laboratories on the cationic polymerization performed in the presence of strong π-electron acceptors will be discussed.

Our first investigations dealt with two monomers: a vinyl monomer (styrene) [1] and a cyclic monomer (trioxane) [2], the polymerization of which was initiated by boron trifluoride diethyl etherate (BFE). It was established that when the polymerization is carried out in a less polar solvent, such as 1,2-ethylene dichloride or carbon tetrachloride, the polymerization rate increases with the addition of electron acceptors (EA) to the reaction mixture in quantities which are commensurate with the initiator concentrations (Figs. 1 and 2). The increase of the polymerization rate is proportional to the electron affinities of the EA used (Fig. 3) [2]. The rate of polymerization increases with increasing the concentration of EA and the dependence goes through a maximum (Fig. 4) [1].

The experimental data obtained with other monomers such as α-methylstyrene, other styrene derivatives, or indene, as well as with other initiators such as $TiCl_4$, carbenium salts, e.g., $(C_6H_5)_3C^+SbCl_6$, etc. have also shown the acceleration of the cationic polymerization in the presence of EA.

How could one explain the acceleration of the cationic polymerization in the presence of EA? At present only a hypothetic explanation of this effect can be given, but this is based on several important facts.

When the solvent is not an electron donor, a complex is formed between the monomer and the EA, as shown by the appearance of color and the characteristic visible spectra (Fig. 5) [3]. It should be noted that in all cases investigated only one complex is formed corresponding to stoichiometric amounts of the two constituents (mole ratio 1), irrespective of the excess of monomer. The higher the ionization potential of the donor, i.e., the monomer, the higher is the complex stability. The complexes do not have an ionic character; they are molecular complexes.

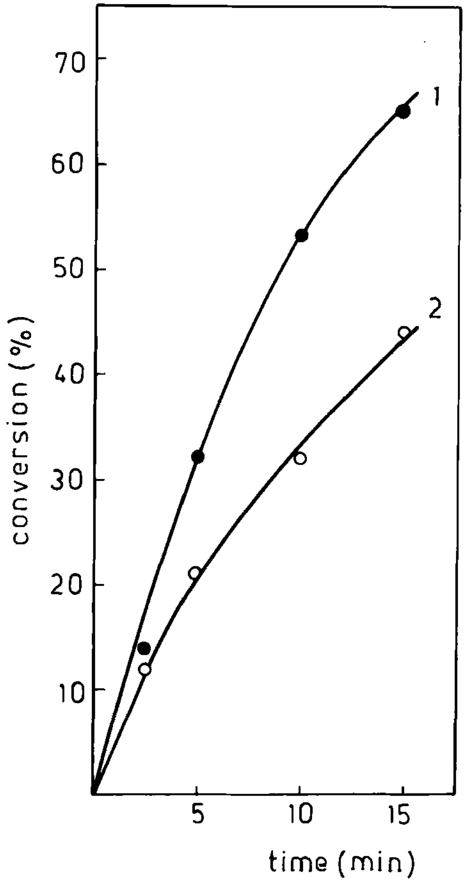


FIG. 1. Polymerization of styrene in 1,2-dichloroethane initiated by BFE: (1) in presence of TCE ([TCE]/[BFE] = 2); (2) no EA. Styrene, 1 mole/liter; BFE, 10^{-2} mole/liter; 20°C [1].

The second important fact is that decomposition of the monomer-EA complex occurs when initiator is added to the monomer-EA solution, as shown by the decoloration of the solution accompanied by the disappearance of the characteristic absorption maximum of the complex (Fig. 6) [4]. In the case of styrene and tetracyanoethylene a five- to sixfold excess of boron trifluoride diethyl etherate is necessary to decompose the complex completely. The decomposition of the styrene-TCE complex after addition of BFE is indicative of the existence of an EA-initiator interaction.

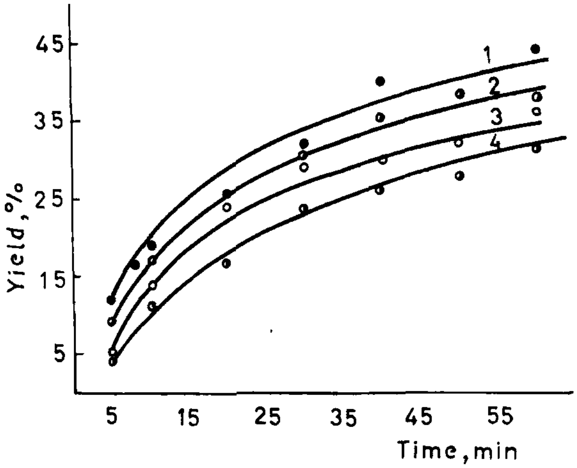


FIG. 2. Polymerization of trioxane in 1,2-dichloroethane initiated by BFE: (1) in presence of TCE; (2) in presence of CA; (3) in presence of TNB; (4) no EA. Trioxane, 3 mole/liter; BFE, 10^{-2} mole/liter; 30° C; [EA]/[BFE] = 12 [2].

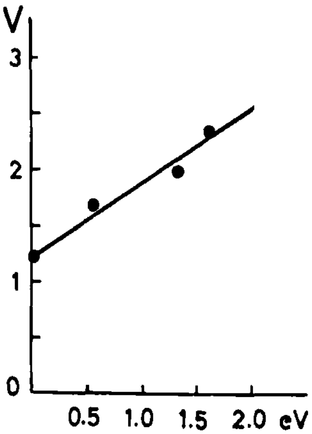


FIG. 3. Rate of trioxane polymerization in 1,2-dichloroethane (see Fig. 2) as a function of the electron affinity of EA [3].

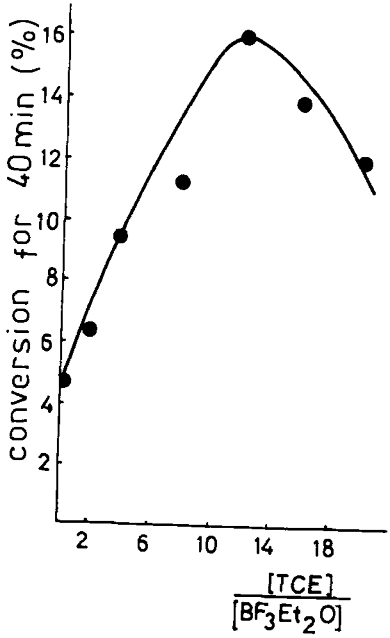


FIG. 4. Polymerization of styrene in the presence of different amounts of TCE. Time 40 min; other conditions as in Fig. 1 [1].

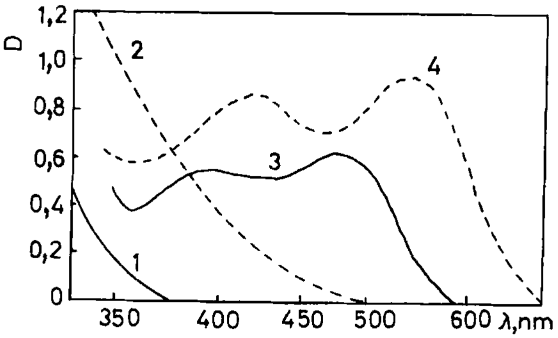


FIG. 5. Visible spectra of monomers and their complexes with TCE in 1,2-dichloroethane at 20°C: (1) styrene; (2) indene; (3) styrene-TCE; (4) indene-TCE [3].

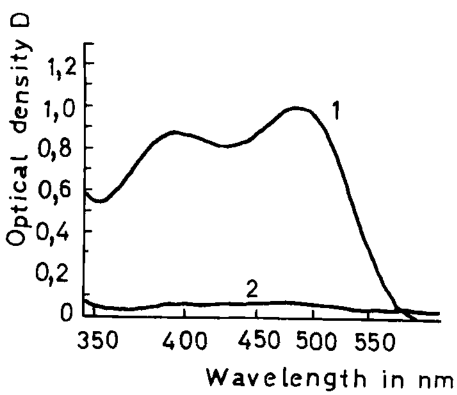


FIG. 6. Visible spectra of (1) the styrene-TCE-complex and (2) the reaction mixture after adding BFE [4].

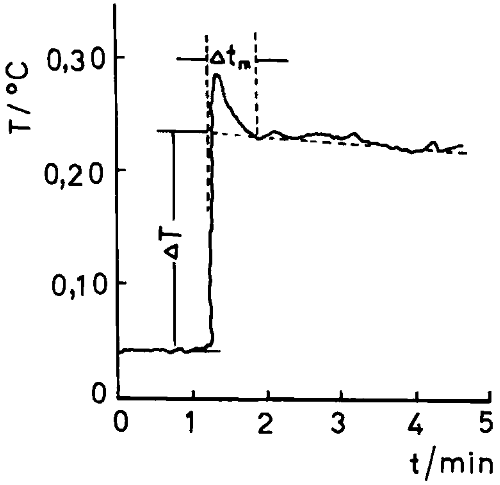


FIG. 7. Calorimetric measurement of formation of TCE-BFE complex in 100 ml 1,2-dichloroethane at 22°C. TCE, 6.25 × 10^{-3} mole/liter; t_m mixing time, ΔT = rate of temperature rise [4].

Direct evidence for the complex formation between EA and initiator, presumably with the initiator counterion, was obtained with an isothermal calorimeter (Fig. 7) [4]. After mixing the TCE and BFE

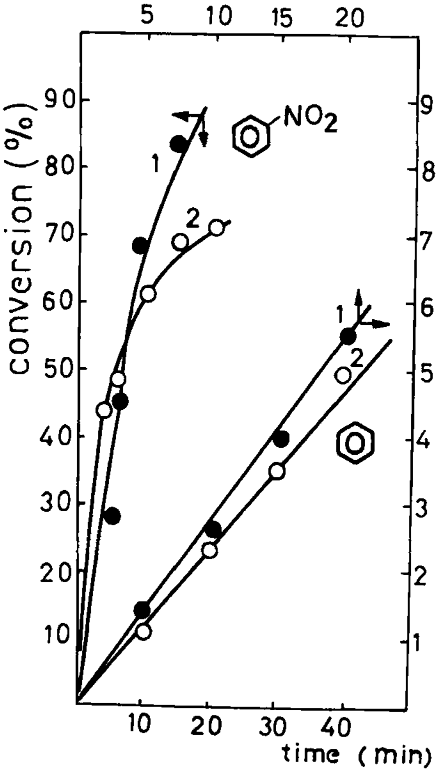


FIG. 8. Polymerization of styrene in benzene and nitrobenzene: (1) in presence of TCE; (2) no EA. Other conditions as in Fig. 1 [1].

solutions, a rise in temperature ($\Delta T = 0.195^\circ C$) was recorded. This is the third important fact which should be taken into account.

The fourth important fact is that the EA effect is not observed in solvents which are electron donors (benzene) or have high dielectric constants (nitrobenzene) (Figs. 8 and 9) [1, 2].

On the basis of the four facts stated the following reactions in the system initiator-monomer-EA are likely to take place:

$$M + EA \rightleftharpoons [M \ldots EA] \qquad (1)$$

$$In^+B^- + [M \ldots EA] \rightleftharpoons InM^+[B \ldots EA]^- \qquad (2)$$

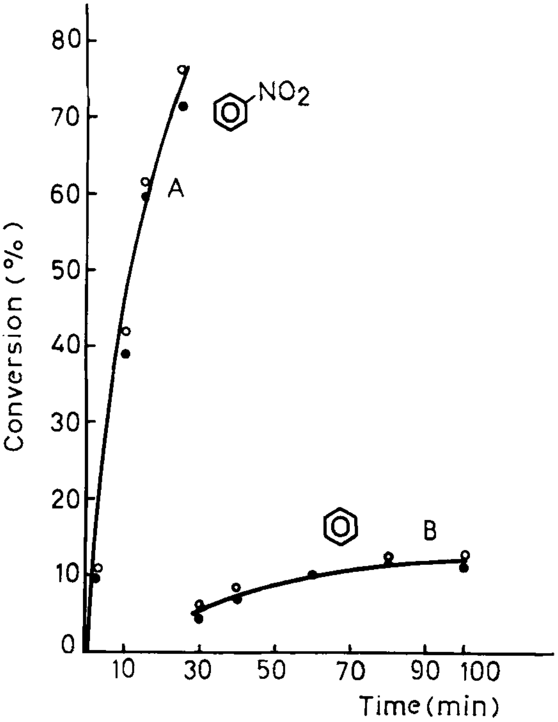


FIG. 9. Polymerization of trioxane in (B) benzene and (A) nitrobenzene: (○) in presence of TCE; (●) no EA. Other conditions as in Fig. 2.

Reaction (1) is indicated by appearance of color and a characteristic visible spectrum; reaction (2) is a decomplexation. Thus the charge of the negative counterion is delocalized over the complex formed between the EA and the counterion.

The complex decomposition expressed by the Eq. (2) should take place when the interaction between the EA and the counterion is stronger than that between EA and monomer. In Table 1 are represented the stability constants of some TCE complexes with different monomers and counterions.

The stability constants of the monomer-EA complexes were determined by the spectral method of Benesi and Hildebrand [3] and those of the counterion-EA complexes with an isothermal calorimeter [5]. The values of the stability constants of the EA-counterion complexes are, without exception, higher than those of the EA-monomer complexes.

In order to reveal the mechanism of cationic polymerization in the

TABLE 1. Stability Constants K_s of TCE Complexes with Monomers and Counterions in 1,2-Dichloroethane [3, 5]

Donor	T (°C)	K_s (liter/mole)
4-Vinylcyclohexene-1[a]	25	0.11
Styrene	20	0.80
Indene	20	1.12
p-Methylstyrene	20	2.00
α-Methylstyrene	20	3.18
SbF_6^-	25	6.7
AsF_6^-	25	7.0
$SbCl_6^-$	25	26.0
$TiCl_5^-$	25	38.0

[a] In methylene chloride.

presence of EA we investigated the kinetics of the styrene polymerization initiated by boron trifluoride diethyl etherate [4]. It was established that the presence of EA does not change the kinetic scheme of the reaction. The overall polymerization rate is expressed by the kinetic equation, $V = K[M]^2$, where [M] is the styrene concentration and K is the rate constant. The external orders with respect to the monomer and the initiator, i.e., the relations $\log V_0 - \log [M]_0$ and $\log V_0 - \log [I]_0$, do not change in the presence of EA (Fig. 10). This was observed in a wide concentration range, from $[M] = 0.1$ to 1.0 mole/liter for styrene, indene, etc. The calculated values of K and the activation energies E are represented in Table 2 [4].

Under the same conditons ([EA] = [TCE]) the values of K in the polymerization of indene are 1.06×10^3 and 1.63×10^3, respectively [6]. It could be expected that the rate of initiation will also increase in the presence of EA. This assumption, however has not been confirmed so far. The values of the initiation constants in the α-methylstyrene polymerization initiated by $(C_6H_5)_3C^+ FeCl_4^-$ or $(C_6H_5)_3C^+SbCl_6^-$ are only insignificantly affected by the presence of TCE [6].

The change in anion size in the presence of EA as well as the delocalization of the electron charge of the counterion increases the

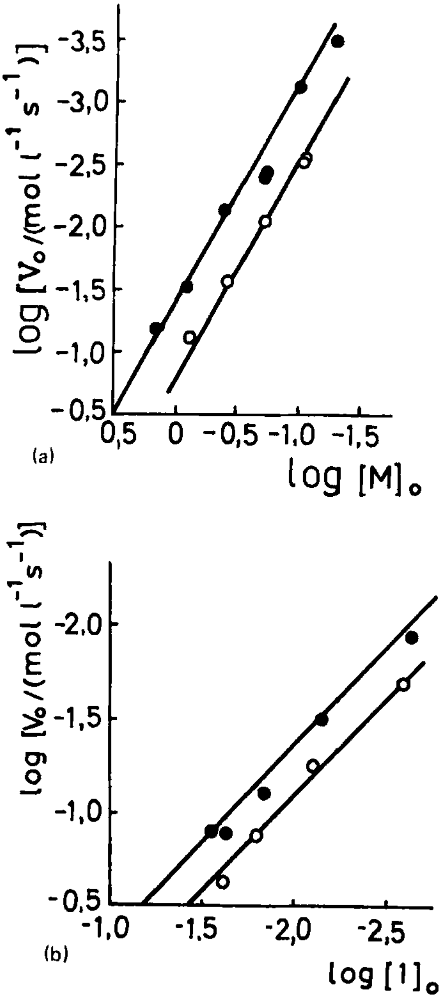


FIG. 10. Dependence of the initial rate of polymerization V of styrene (●) in absence and (○) in presence of TCE on the initial concentrations of (a) monomer and (b) initiator. [TCE] = 8 × 10^{-3} mole/liter; (b) styrene 0.8 mole/liter [4].

TABLE 2. Values of K and E for Polymerization of Styrene in the Absence and Presence of EA[a]

Polymerization conditions	$K \times 10^{-3}$	E (kcal/mole)
No EA	0.13	11.4
In presence of TNB	0.25	-
In presence of TCE	0.34	6.9

[a] $[BFE] = [EA] = 2.5 \times 10^{-3}$ mole/liter, $[M] = 1$ mole/liter; 20°C; 1,2-dichloroethane.

dissociation constant and therefore the concentration of free ions. The following reaction mechanism seems to be the most probable [4].

Without EA:

$$\ldots\text{-}P^{+}X^{-} \overset{K_D}{\rightleftharpoons} \ldots\text{-}P^{+} + X^{-}$$

In the Presence of EA:

$$\ldots\text{-}P^{+}[X\ldots EA]^{-} \overset{K_D^{EA}}{\rightleftharpoons} \ldots\text{-}P^{+} + [X\ldots EA]^{-}$$

$$K_D^{EA} > K_D$$

Indeed, it was found that the values of the dissociation constants in the presence of EA are higher than in the absence of EA (Table 3).[7].

Addition of TCE to the polymerizing system styrene-BFE brings about an increase in the specific conductivity of the system (Fig. 11) [4].

In all cases studied so far, an increase in the molecular weights of the polymers obtained in the presence of EA was recorded. The dependence of the molecular weights on the EA amount always passes through a maximum. This was established in the polymerization of ethylene initiated by $AlBr_3/SbCl_5$ (Fig. 12) [8, 9], in the polymerization of styrene, indene, and trioxane initiated by BFE (Fig. 13) [10] and in the polymerization of norbornene by $AlCl_3$ (Table 4) [11, 12].

TABLE 3. Dissociation Constants of Boron Trifluoride Diethyl Etherate in the Presence and in Absence of EA[a]

Reaction conditions	$K_D \times 10^9$
No EA added	1.64
In presence of TNB	2.88
In presence of TCE	3.25

[a] [BFE]: [EA] = 1; 1,2-dichloroethane; 10°C [7].

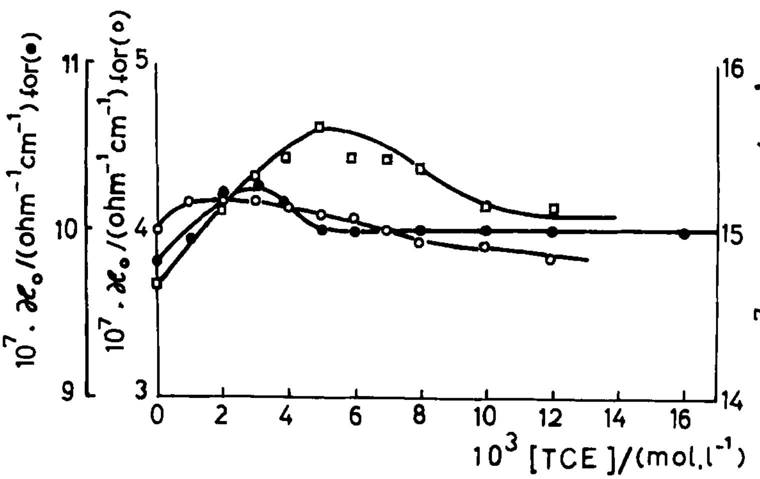


FIG. 11. Dependence of the specific conductivity x on the concentration of TCE at different initial BFE concentrations: (○) 8×10^{-3}, (●) 10×10^{-3}, (□) 24×10^{-3} mole/liter. Styrene 0.8 mole/liter [4].

The increase of the overall polymerization rate can be explained by assuming a change in the rates of the elementary reactions (initiation, chain propagation, termination, and chain transfer). The established increase in the molecular weights in the presence of EA shows that the effect of the EA should be attributed mainly to the increase in the rate of propagation. The equilibrium expressed by Eq. (2) leads to an ion pair separated by EA, which causes a more rapid chain propagation than a contact ion pair. The reason is probably the increased electrophilic nature of the chain carrier due to the

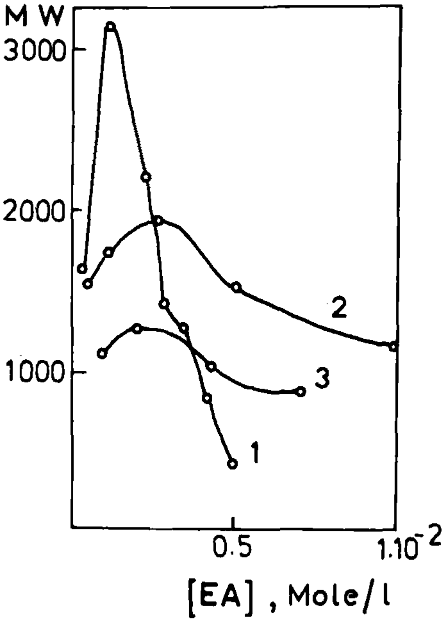


FIG. 12. Effect of EA on molecular weights in the polymerization of ethylene: (1) TCE; (2) tetracyanoquinodimethane; (3) CA. $AlBr_3/SbCl_5$ 1.05 × 10^{-1}/0.6 × 10^{-2} mole/liter methylene chloride; -50°C [8, 9].

larger charge separation in the "EA separated ion pair". In the case of styrene polymerization it was found that chain transfer is unimportant, regardless of the presence or the absence of EA (Fig. 14) [10].

The molecular weight decrease after reaching the maximum (Figs. 12 and 13 and Table 4) does not clearly depend on the nature of the monomer and the reaction conditions (solvent, temperature, initiator).

In the qualitative approach of the EA effect one can assume that the stationary counterion concentration is rather low as compared with the initiator concentration. This argument is corroborated by the fact that the initiator efficiency is in the range of 1 to 30% when Lewis acids are used as initiators [13]. Because of this, the acceptor concentration necessary for the formation of EA separated ion pairs [Eq. (2)] should be very low. The latter accounts for the rapid reaching of the maximum. At higher EA concentrations, the complex formation will be favored according to Eq. (1). The resulting decrease

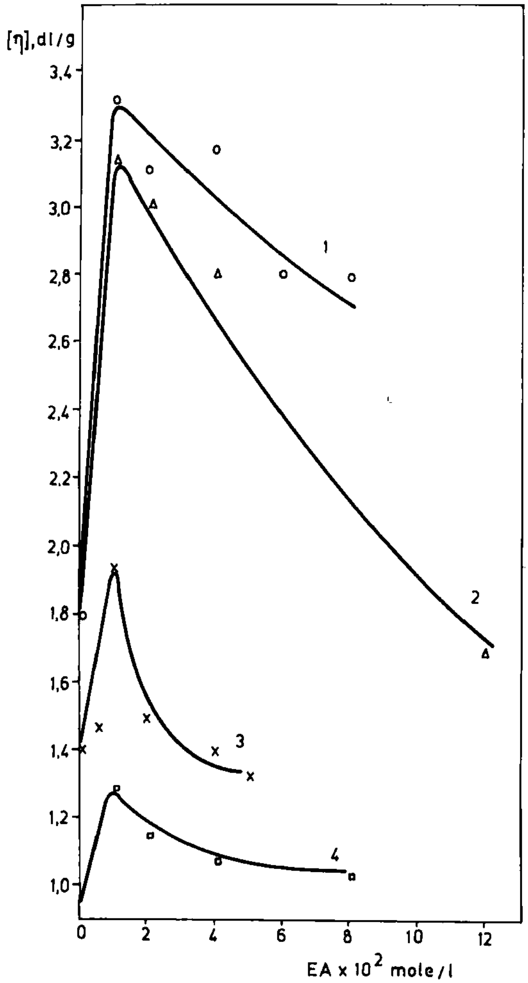


FIG. 13. Dependence of intrinsic viscosity on quantity of EA added: (1) styrene (1 mole/liter)-TNB, BFE (10^{-2} mole/liter), 1,2-dichloroethane, 0° C; (2) styrene-1-chloro-2,4-dinitrobenzene, same conditions; (3) indene-TCE, 20° C, same conditions; (4) trioxane-TCE, BFE, bulk polymerization in the melt, 70° C.

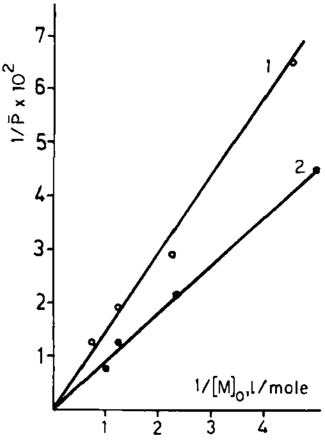
TABLE 4. Dependence of Molecular Weights of Polynorbornene on EA Concentration[a]

Electron acceptor		Molecular weight	Melting range of the polymer (°C)
Type	Concn (mole/liter)		
None	0	645	136-137
Chloranil	1.64×10^{-3}	1390	163-180
	4.36×10^{-3}	1560	164-185
	7.01×10^{-3}	1720	187-197
	1.35×10^{-2}	1450	167-176
	1.50×10^{-2}	1200	167-170
Tetracyano-ethylene	1.96×10^{-3}	740	143-157
	2.81×10^{-3}	980	147-161
	6.46×10^{-3}	3285	240-260
	9.64×10^{-3}	1600	161-181
	1.07×10^{-2}	1440	163-176
	1.76×10^{-2}	1050	140-163

[a] Initiator $AlCl_3$, 5×10^{-2} mole/liter; 1,2-dichloroethane, -20° C.

in the "efficient" monomer concentration will probably lead to retarded chain growth [11, 12]. Of course, further investigations are necessary for better understanding of this phenomenon.

It might be expected that the presence of EA will also affect the relative reactivity of the monomers in the copolymerization. Indeed, such a change was established in all cases investigated. The initial rates of copolymerization of both comonomers increase but to different degrees, regardless of the monomer ratio in the reaction mixture (Fig. 15) [14]. For most of the reactions investigated the presence of EA favors the insertion of less reactive monomer. This was the case in the copolymerization of the monomer pairs styrene-α-methylstyrene (Fig. 15), vinylcyclohexane-β-methylstyrene (Fig. 16) [15-17], and trioxane-dioxolane in the melt [14]. The effect of the EA added on the copolymer composition is particularly pronounced in the copolymerization of styrene and isobutyl vinyl ether (Tables 5 and 6) [11, 12, 18].



$$\frac{1}{\bar{P}} = \frac{K_t}{K_p[M]_0} + \frac{K_{tm}}{K_p} + \frac{K_{ts}}{K_p}\frac{[S]}{[M]}$$

FIG. 14. Dependence of the degree of polymerization on the initial styrene concentration: (1) no EA; (2) in presence of TCE, 10^{-2} mole/liter. BFE 10^{-2} mole/liter, 1,2-dichloroethane, 20°C [10].

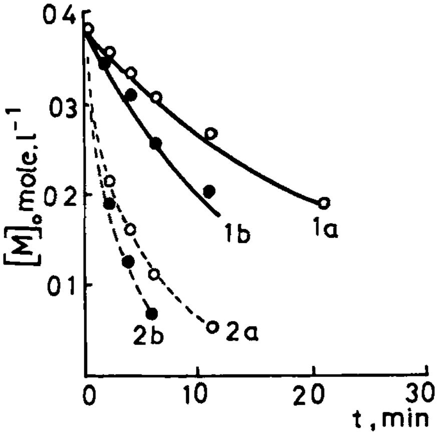


FIG. 15. Kinetic curves of the copolymerization of styrene (M_1)-α-methylstyrene (M_2) pair: (a) no TCE; (b) in presence of TCE. Initiator BFE, 8×10^{-3} mole/liter; TCE, 8×10^{-3} mole/liter; 1,2-dichloroethane, 7°C [14].

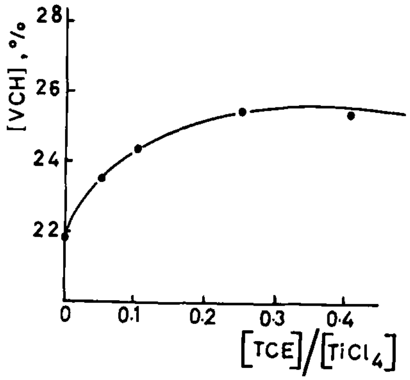


FIG. 16. Effect of TCE added on the quantity of vinylcyclohexane units (VCH) in the vinylcyclohexane-β-methylstyrene copolymer. Initiator $TiCl_4$, 6 × 10^{-3} mole/liter, methylene chloride, 0°C [15].

TABLE 5. Effect of Chloranil Added on the Quantity of Styrene Units in the Styrene (M_1)-isobutyl Vinyl Ether (M_2) Copolymer[a]

Chloranil added (mole/liter)	Styrene units in copolymer (mole %)
0	11.5
6.70×10^{-5}	18.5
2.03×10^{-4}	28.0

[a] $[M_1]:[M_2] = 9$; initiator, $TiCl_4$, 6×10^{-3} mole/liter; chloroform; -40°C; conversion 10%.

It is seen that the initial monomer ratio also contributes to the EA effect, as is evident from the data shown in Tables 7 and 8 [11, 12, 18].

The results represented in Table 9 show that the change in the solvent and the EA concentration result in a different copolymer composition [15-17].

The preparation of a more thermostable polymer which at the same time has a higher molecular weight in the iodine catalyzed copolymerization of trioxane and dioxolane can be probably attributed to the electron acceptor character of the iodine [19].

TABLE 6. Effect of Tetracyanoethylene Added on the Quantity of Styrene Units in the Styrene (M_1)-Isobutyl Vinyl Ether (M_2) Copolymer[a]

Tetracyanoethylene added (mole/liter)	Styrene units in copolymer (mole %)
0	18
1.3×10^{-4}	30
3.9×10^{-4}	40

[a] $[M_1]:[M_2] = 7:3$; initiator, $AlCl_3$, 2.4×10^{-3} mole/liter; ethyl bromide; -78°C; conversion 1%.

TABLE 7. Composition of the Styrene-Isobutyl Vinyl Ether Copolymers at Different Monomer and Constant EA Concentrations[a]

		Electron acceptor		
Styrene (mole/liter)	IBVE (mole/liter)	TCE (1.04×10^{-3} mole/liter)	CA (0.35×10^{-3} mole/liter)	Styrene units in copolymer (mole %)
0.9	0.1	-	-	33
0.9	0.1	+	-	88
0.9	0.1	-	+	72
0.7	0.3	-	-	20
0.7	0.3	+	-	67
0.7	0.3	-	+	62
0.5	0.5	-	-	5
0.5	0.5	+	-	18
0.5	0.5	-	+	3

[a] Initiator, $AlCl_3$, 2.4×10^{-3} mole/liter; ethyl bromide; -78°C; conversion 1-5%.

TABLE 8. Effect of the Electron Affinity of EA on the Composition of the Styrene-Isobutyl Vinyl Ether Copolymer[a]

Styrene (mole/liter)	IBVE (mole/liter)	EA Type	EA Concn (mole/liter)	Styrene units in copolymer (mole %)
0.95	0.05	None	-	54.5
0.95	0.05	SO_2	1.2×10^{-3}	56.5
0.95	0.05	CA	1.3×10^{-3}	60.5
0.95	0.05	TCE	1.3×10^{-3}	69.5
0.90	0.10	None	-	21.0
0.90	0.10	SO_2	1.2×10^{-3}	22.0
0.90	0.10	CA	1.3×10^{-3}	31.5
0.90	0.10	TCE	1.3×10^{-3}	33.0
0.85	0.15	None	-	11.5
0.85	0.15	SO_2	1.2×10^{-3}	13.0
0.85	0.15	CA	1.3×10^{-3}	16.0
0.85	0.15	TCE	1.3×10^{-3}	18.0
0.80	0.20	None	-	2.0
0.80	0.20	SO_2	1.2×10^{-3}	4.0
0.80	0.20	CA	1.3×10^{-3}	8.5
0.80	0.20	TCE	1.3×10^{-3}	11.0

[a] Initiator, $AlCl_3$, 2.4×10^{-3} mole/liter; ethyl bromide, -78°C; conversion 1-5%.

Tables 10 and 11 show the influence of TCE on the copolymerization constants of the following monomer pairs: styrene-α-methylstyrene [10], styrene-indene [10], and styrene-β-methylstyrene [15-17].

The results obtained so far indicate that in the presence of EA the equilibria (5)-(7), present to a different degree, should be taken into account.

$$M_1 + EA \rightleftharpoons [M_1 \ldots EA] \tag{5}$$

TABLE 9. Copolymerization of Vinylcyclohexane (M_1) and p-Chlorostyrene (M_2) in the Presence of TCE[a]

$[M_1]:[M_2]$	Solvent	Vinylcyclohexane units (%) in copolymer at Various TCE initiator ratios				
		0	0.05	0.15	0.25	0.40
1:1	CCl_4	11.4	12.8	13.8	14.1	14.2
2:1	CCl_4	18.4	20.0	21.3	21.3	21.8
1:1	CH_2Cl_2	12.5	13.9	14.3	14.4	-
2:1	CH_2Cl_2	20.0	21.8	22.3	22.6	22.5

[a] Initiator, SnCl , 8×10^{-3} mole/liter in CCl_4 or 6×10^{-3} mole/liter in CH_2Cl_2; 0°C. Vinylcyclohexane units determined by NMR spectroscopy [15-17].

TABLE 10. Effect of Added Tetracyanoethylene on Copolymerization Constants.

M_1	M_2	TCE (mole/liter)	r_1	r_2	r_1r_2
Styrene	α-Methylstyrene	0	0.65 ± 0.22	5.86 ± 0.32	3.8
Styrene	"	8×10^{-3}	0.28 ± 0.08	3.78 ± 0.43	1.06
Styrene	Indene	0	0.73 ± 0.35	3.20 ± 0.72	2.33
Styrene	"	8×10^{-3}	1.57 ± 0.36	3.28 ± 0.52	5.15

[a] Experimental conditions as in Fig. 15 [10].

$$M_2 + EA \rightleftharpoons [M_2 \ldots EA] \qquad (6)$$

$$\ldots P^+X^- + EA \rightleftharpoons \ldots P\ [EA \ldots X]^- \qquad (7)$$

At low EA concentrations the charge separation (solvent-separated ion pair) expressed by the Eq. (7) will have the same effect as an increase in the initiator activity or in the solvent polarity, i.e., a decrease in the selectivity of the active center. As a result, the

TABLE 11. Effect of Added Tetracyanoethylene on the Copolymerization Constants in the Copolymerization of Styrene (M_1) and β-Methylstyrene (M_2)[a]

[TCE]/[$SnCl_4$]	r_1	r_2
0	1.88	0.115
0.025	1.82	0.12
0.20	1.60	0.14
0.50	1.55	0.16

[a] Initiator $SnCl_4$; methylene chloride; 0° C.

monomer of lower reactivity could be favored in the cross reaction of propagation. At higher EA concentration the latter will interact more strongly with the monomer which is the stronger electron donor, i.e., with the more reactive monomer in the polymerization reaction. The decrease in "efficiency" caused by the complex formation will also favor the less reactive monomer. In general, in the presence of EA an approach in the relative monomer reactivities results due to the specific reactions between the reaction components [20].

SUMMARY

The phenomenological aspect of the electron-acceptor effect on the cationic polymerization of vinyl and cyclic monomers is discussed. It is established that the presence of electron acceptors has a definite influence on the polymerization and the copolymerization of all monomers studied. The electron acceptors added to the system accelerate the polymerization and cause an increase in the molecular weights of the polymers obtained. They affect the course of the copolymerization by lowering the selectivity of the active centers. In other words, strong electron acceptors offer a possibility for controlling the cationic polymerization and copolymerization. An attempt is made to explain the effect of electron acceptors which still have a hypothetical character. To clarify the problem, more precise quantitative investigations on the phenomena observed are necessary. The best way to study the donor-acceptor interactions is to study the behavior of similar model systems; such investigations are now being carried out in our laboratories.

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