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Studies of Radical Alternating Copolymerization. III. Kinetics of the Copolymerization of Citraconic Anhydride and Vinyl Acetate: A New Method of Evaluating the Kinetics Constant

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Studies of Radical Alternating Copolymerization. III. Kinetics of the Copolymerization of Citraconic Anhydride and Vinyl Acetate: A New Method of Evaluating the Kinetics Constant

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ABSTRACT

We show that the copolymerization of citraconic anhydride and vinyl acetate is an alternating one. The two monomers form a charge transfer complex, and we propose a new strategy to determine the value of the velocity constants $\beta_1 = K_{AC}/K_{AD}$ and $\beta_2 = K_{DC}/K_{DA}$ involving the acceptor A, the donor D, and their charge transfer complex C. We obtained $\beta_1 = 9.9$ and $\beta_2 = 3.6$. The complex exhibits a greater reactivity than the monomer in the propagation reactions.

INTRODUCTION

The mechanism of alternating radical copolymerization has often been investigated [1]. In previous papers we studied the alternating copolymerization of maleic anhydride and vinyl acetate [2-5]. In

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this case the mechanism of copolymerization involves the participation of both free monomers and of a complex between them. We have paid attention to:

1. The influence of the complex on the reaction kinetics [2, 5]
2. The conformation [3] and the relative reactivity [3, 5] of the complex
3. The influence on the microstructure of the alternating copolymers on the participation of the complex in propagation reactions [4]

EXPERIMENTAL

Materials

Vinyl acetate was purified according to a procedure described in the literature [6]. Citraconic anhydride (2,5-furanedione, 3-methyl) was a commercial reagent (Janssen). α,α'-Azobisisobutyronitrile (AIBN) was recrystallized from ethyl alcohol and then dried under vacuum. All solvents were purified using standard procedures just before use.

Polymerization

Pyrex polymerization vessels were charged with known quantities of freshly purified monomers, initiator, and solvent. After connection to a high vacuum line, their contents were degassed, and then the vessels were sealed. The vessels were maintained during the time of polymerization in a thermostat adjusted to ±0.1°C. The polymerization was stopped at low conversion (maximum, 10%) by a quick cooling of the polymerization vessel. The crude copolymers were precipitated in n-hexane and purified by successive dissolution in tetrahydrofuran and precipitation in n-hexane. Then the copolymers were dried under vacuum until constant weight. The copolymerization rates, defined by $R_p = -(d/dt)([A] + [D])$, were obtained by the gravimetric method.

Spectrometric Studies

The UV spectra were recorded at 25°C from a Beckman DGB spectrophotometer using 1 cm quartz cells. The ^{1}H-NMR spectra were obtained with a Varian T 60 spectrometer using TMS as the internal reference and cyclohexane as the solvent. IR spectra were recorded from films with a Perkin-Elmer 257 IR spectrophotometer.

Functional Analysis

The anhydride functions in the copolymeric chain were titrated at room temperature from solution in a mixture of water and acetone by a conductimetric method [7] using a Wayne Kerr autobalance universal bridge B641.

RESULTS AND DISCUSSION

Copolymer Structure

In the following text, A refers to acceptor citraconic anhydride and D to donor vinyl acetate. Table 1 collects the results of the determination of the molar ratio f_A of citraconic anhydride in copolymers as a function of its initial molar ratio F_{A_0} in the feeding mixtures.

Within experimental error, an equimolecular copolymer was always obtained irrespective of the monomer feed ratio and the total initial comonomer concentration M_0. Starting from the fact that citraconic anhydride does not homopolymerize under our experimental condition, we conclude that alternating copolymers were obtained. The chemical structure of the copolymers was confirmed by IR and ^{1}H-NMR spectra. Figure 1 shows a typical IR spectrum of the alternating copolymers. This spectrum exhibits the characteristic peaks at 1870 and 1790 cm^{-1} of the anhydride ring and at 1740 cm^{-1} of the ester function. Figure 2 shows the ^{1}H-NMR spectrum of the copolymer and the assignment of the resonance. The composition of the copolymers was confirmed from ^{1}H-NMR by comparison with 2.17 and 1.68 ppm resonances (results reported in Table 1).

Study of the Complex between Comonomers

The formation of a complex C between comonomers A (citraconic anhydride) and D (vinyl acetate) is governed by Equilibrium (1). K is the equilibrium constant defined by Eq. (2).

$$A + D \rightleftharpoons C \tag{1}$$

$$K = [C]/([A][D]) \tag{2}$$

This formation induces some variations in the properties of the solution, especially a modification of the UV spectrum [8] (a new

TABLE 1. Composition of the Copolymers vs the Composition of the Feeding Mixtures

Copolymerization in benzene, t = 60°C					Copolymerization in THF; M_0 = 2 mol/L		
	M_0 = 2 mol/L		M_0 = 4 mol/L				
F_{A_0}	f_A[a]	f_A[b]	f_A[a]	f_A[b]	F_{A_0}	t = 60°C, f_A[a]	t = 70°C, f_A[a]
0.1	0.507	0.516	0.503	0.490	0.10	0.500	
0.2	0.503	0.510	0.510	0.523	0.15	0.497	0.503
0.3	0.497	0.510	0.505	0.477	0.20	0.497	0.503
0.4	0.502	0.515			0.30	0.497	0.506
0.5	0.501				0.40		0.503

[a] Chemical determination.
[b] ^{1}H-NMR determination.

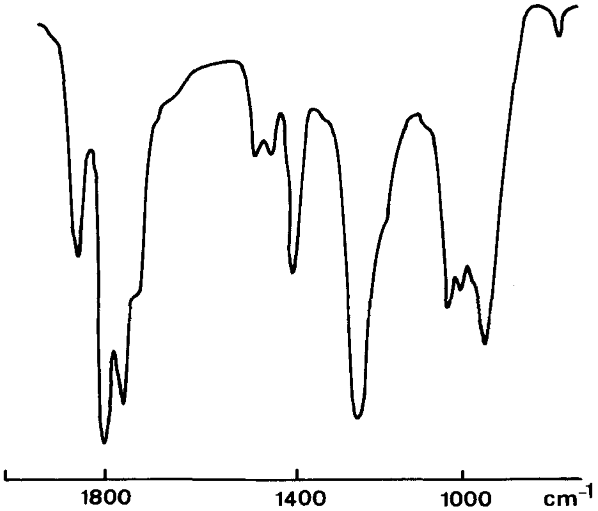

FIG. 1. Infrared spectrum of alternating copolymers.

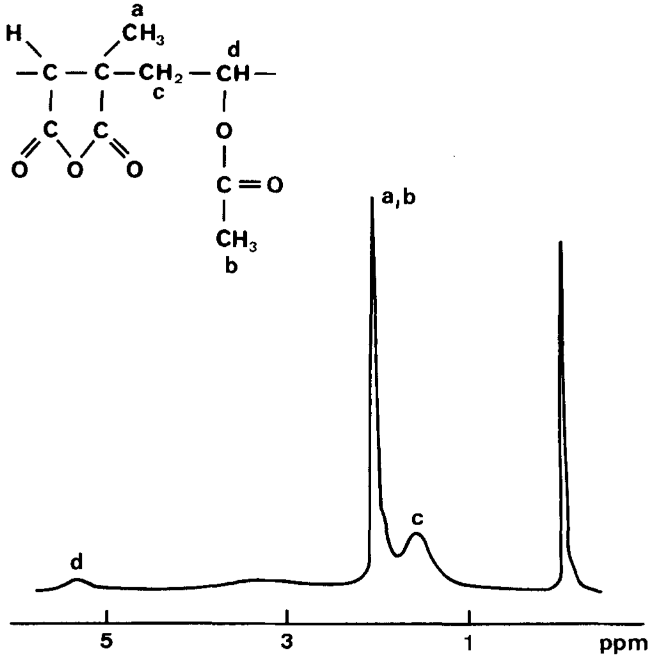

FIG. 2. ^{1}H-NMR spectrum of alternating copolymers, attributed to resonance. Solvent: Pyridine. TMS as the internal standard.

absorption band or a variation of the molar extinction coefficients), and a shift of the resonances of the A and D protons [9]. We applied the last method to evaluate the constant K of the citraconic anhydride-vinyl acetate system, and we studied the shift of the proton of the A molecule.

Experimental conditions were such as $[D] \gg [A]$, so that D is similar to the initial concentration $[D]_0$. Deranleau [10] has pointed out two conditions for the initial concentration to guarantee valid experimental results. Starting from the saturation fraction defined as $s = [C]/[A]_0$, these conditions are:

1. The sampling concentrations must be in the range $.2 < s < .8$
2. The experimental points must cover 75% of the concentration range defined by 1

The NMR spectrum of the A molecule exhibits a doublet at 2.2 ppm and a quadruplet at 6.6 ppm, attributed respectively to the methyl group and the ethylenic protons. We studied the shift of the ethylenic proton by applying Relation (3) due to Hanna et al. [9]:

$$\frac{1}{[D]_0} = \Delta_c K \frac{1}{\Delta_{obs}} - K \tag{3}$$

$$\Delta_{obs} = \delta^A_{obs} - \delta^A_{fr}; \qquad \Delta_c = \delta_c{}^A - \delta_1{}^A$$

where δ^A_{obs}, δ^A_{fr}, and $\delta_c{}^A$ are the shifts of the A proton observed in a given experiment, in the free form, and in the pure complex, respectively. We studied the A-D system in cyclohexane. The variations of Relation (3) at different temperature are reported in Fig. 3, and the K values are reported in Table 2. At 300 K we obtain $K \simeq .52$ L/mol.

Starting from an Arrhenius plot, we obtain $\Delta H = 5.7$ kJ/mol. Copolymerizations were carried out in benzene and in tetrahydrofuran. Thus, we examined the possibility of a A-benzene complex and a A-tetrahydrofuran complex by the same method. Results are reported in Table 2 and Fig. 4. In the case of the A-benzene complex, we observed only a very weak complex, but in the case of the A-THF complex we have $K_S = .48$ L/mol at 301 K.

Kinetic Analysis of the Copolymerization

Alternating copolymerization involving the participation of a complex between comonomers can be described by the following reactions [1c, 1d, 1e, 2, 5]:

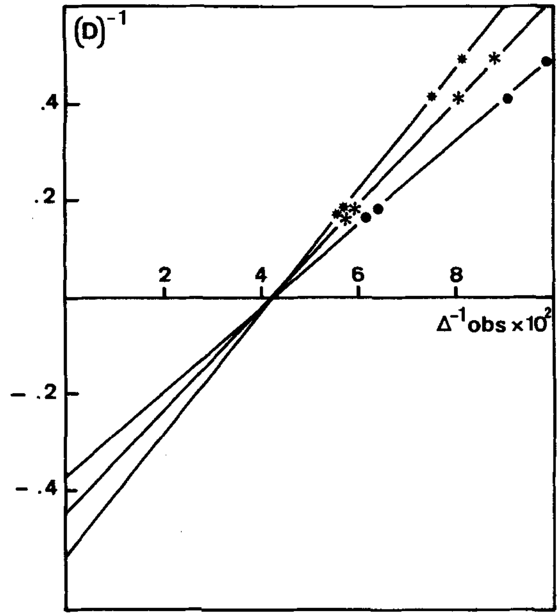

FIG. 3. ^{1}H-NMR determination of the K value of AD formation. Solvent: cyclohexane. (●) 300 K, (*) 308 K, (*) 323 K.

TABLE 2. Values of the Constants of Complexation of Citraconic Anhydride with Various Donor Molecules

	A-D complex			A-THF complex	A-Bz complex
t, °C	27	35	50	28	25
K, L/mol	.52	.44	.37	.48	.05

$$\sim A^\circ + D \xrightarrow{K_{AD}} \sim D^\circ \tag{4}$$

$$\sim D^\circ + A \xrightarrow{K_{DA}} \sim A^\circ \tag{5}$$

$$\sim A^\circ + C \xrightarrow{K_{AC}} \sim A^\circ \tag{6}$$

$$\sim D^\circ + C \xrightarrow{K_{DC}} \sim D^\circ \tag{7}$$

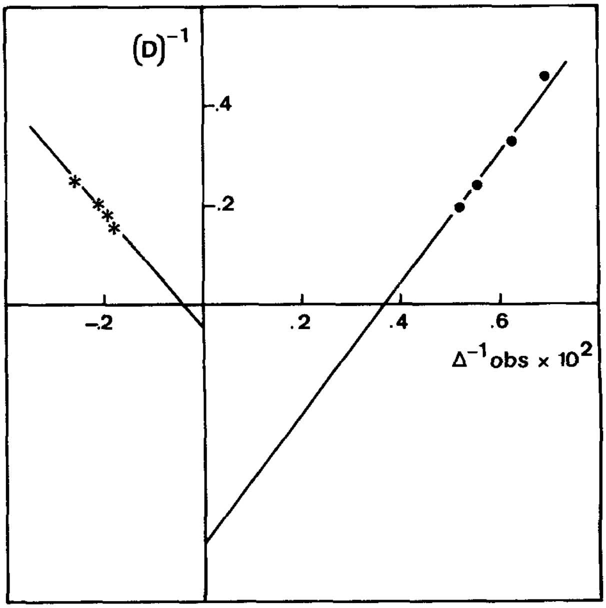

FIG. 4. ^{1}H-NMR determination of the K value of the (●) A-THF complex, (*) A-benzene complex at 301 K.

Some authors [1a, 11] suggest the possibility that only one monomer of the A-D complex adds to the growing chain [8]. In this case we have steps

$$\sim A^\circ + C \longrightarrow \sim D^\circ + A \qquad (8)$$

$$\sim D^\circ + C \longrightarrow \sim A^\circ + D \qquad (9)$$

To date these possibilities have not been investigated, so we opt for the classical scheme (4)-(7).

Some methods have been developed in the literature for kinetic analysis of the data. These methods can be classified in two categories:

1. The kinetic analysis is based on a study of the overall rate of polymerization upon the molar fraction [1e, 12] of the donor.
2. The kinetic analysis is based on the variation of the position of the maximum of the copolymerization rate vs the total monomer concentration [1e, 2, 5].

The rate of the copolymerization is given by

$$R_p = K_{AD}\left(\frac{R_i}{K_{to}}\right)^{0.5} \frac{[A]([D] + 2\beta_1[C]) + [D]([A] + 2\beta_2[C])}{\alpha[D] + [A]} \qquad (10)$$

where [i] is the concentration of species i in the reactive medium and

$$\alpha = K_{AD}/K_{DA} \qquad \beta_1 = K_{AC}/K_{AD} \qquad \beta_2 = K_{DC}/K_{DA}$$

R_i is the initiation rate and K_{to} is the constant of the bimolecular termination, assuming that termination is diffusion-controlled [1e, 5].

Depending on the essential characteristics of the alternating copolymerization, four cases will be discussed for the determination of constants α, β_1, and β_2 [1e].

1. Equilibrium constant K of complex formation is very small and the initiation rate is constant
2. Equilibrium constant K is not small and the initiation rate is constant
3. Equilibrium constant K is small, but the initiation rate is not constant
4. Equilibrium constant K is not small and the initiation rate is not constant

In our case the constant K is not small (K_{300} = .52) and we have no information on the initiation rate. If we used a method based on the variation of the position of the maximum of the copolymerization rate vs the total monomer concentration, we could not account for a possible variation of R_i vs the composition of the mixture of comonomers. The three constants necessitate the determination of three maximum copolymerization rates. The calculation proposed by Georgiev et al. [1e] is very difficult. We proposed a new strategy to obtain the values of the constants. Starting from Eq. (10) and

1. Introducing the total monomer concentration M = [A] + [D] <u>in the reactive medium and at the experimental temperature</u>
2. Making the assumption that $\alpha = K_{AD}/K_{DA} \simeq 0$ (this assumption can be justified by the much greater reactivity of radical ~D° [1e, 5]

We can deduce

$$R_p = 2k_{AD}\left(\frac{R_i}{K_{to}}\right)^{0.5}[(1 - F_A)M + \beta_1 K(1 - F_A)M^2 + \beta_2 K(1 - F_A)^2 M^2] \qquad (11)$$

where F_A is the ratio [A]/([A] + [D]).

Under this condition the position of the maximum $(F_A)_{max}$, obtained by solving $\partial R_p/\partial F_A = 0$, is given by

$$(F_A)_{max} = \frac{\beta_1 - 2\beta_2}{2(\beta_1 - \beta_2)} - \frac{1}{\beta_1 - \beta_2}\,\frac{1}{2K}\,\frac{1}{M} \qquad (12)$$

β_1 and β_2 can be determined either from Relation (12) or by the linear equations [5]

$$\tfrac{1}{2}M(0.5 - (F_A)_{max}) = \beta_1 K - \beta_2 K\,\frac{1 - (F_A)_{max}}{0.5 - (F_A)_{max}} \qquad (13)$$

$$\tfrac{1}{2}M(1 - (F_A)_{max}) = \beta_1 K\,\frac{0.5 - (F_A)_{max}}{1 - (F_A)_{max}} - \beta_2 K \qquad (14)$$

When the concentration of the charge transfer complex between comonomers is very low, its propagation rate can be neglected. In this case the rate of alternating copolymerization is given by the relation [2]

$$R_p = 2K_{AD}\left(\frac{R_i}{K_{to}}\right)^{0.5}[(1 - F_A)M] \qquad (15)$$

which is linear vs F_A.

Application to the AC/AV System

Copolymerization in Benzene

In benzene the dependence of the copolymerization rate on the square root of the initiator concentration [I] is linear (Fig. 5). This

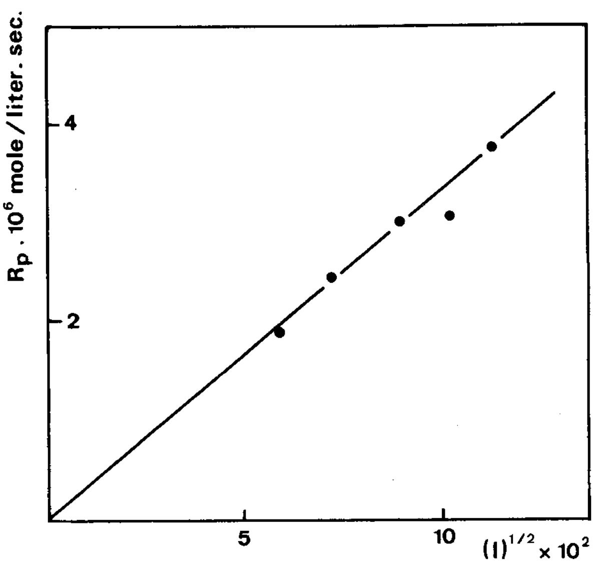

FIG. 5. Dependence of R_p vs initiator concentration. Solvent: benzene. 60°C. $[A]_0 = 0.4$ mol/L, $[D]_0 = 1.6$ mol/L.

dependence suggests the presence of bimolecular termination. Starting from the values of the equilibrium constant K and ΔH, we can evaluate the value of K at the temperature of copolymerization (333 K): $K_{333} = .32$ L/mol.

We can now calculate the experimental condition (we neglect the A-Bz complex). We have $M = [A] + [D]$, $[A] = F_A M$, $[D] = (1 - F_A)M$, and $[C] = KF_A M(1 - F_A)M$. Thus $A_0 = [A] + [C]$ and $D_0 = [D] + [C]$, where A_0 and D_0 are the initial concentrations of the comonomers and [A], [D], and [C] are the concentrations of the free comonomers and the complex, respectively. The different concentrations studied and the corresponding copolymerization rate are reported in Table 3. The variation of R_p vs F_A is reported in Fig. 6. We obtained a maximum of the rate at a higher [D] in the reactive medium. The position of the maximum depends on the total concentration of comonomers M. These results agree with the kinetic analysis described above.

Starting from the variation of Relation (12) reported in Fig. 7, we can determine the values of β_1 and β_2. We obtained $\beta_1 = 9.9$ and $\beta_2 = 3.6$, $k_{AC} \simeq 10k_{AD}$, and $k_{DC} \simeq 4k_{DA}$. The complex exhibits a greater reactivity than the monomer in the propagation reaction.

TABLE 3. Copolymerization of the AC/AV System at 60°C in Benzene at [A] + [D] = Constant: Experimental Conditions and Rate of Copolymerization

[A], mol/L	[D], mol/L	[C], mol/L	M	F_A	A_0	D_0	$R_p \times 10^6$, mol/L·s
0.033	1.617	0.017	1.65	0.02	0.05	1.630	1.4
0.049	1.600	0.025	1.65	0.03	0.074	1.625	2.02
0.082	1.567	0.041	1.65	0.05	0.123	1.608	2.90
0.115	1.534	0.056	1.65	0.07	0.381	1.50	4.4
0.264	1.386	0.117	1.65	0.26	0.596	1.39	2.25
0.060	1.940	0.0372	2	0.03	0.097	1.977	3.40
0.100	1.900	0.0608	2	0.05	0.160	1.960	4.90
0.160	1.840	0.094	2	0.08	0.254	1.934	5.67
0.200	1.800	0.115	2	0.10	0.315	1.915	5.2
0.300	1.700	0.163	2	0.15	0.463	1.863	4.73
0.400	1.600	0.204	2	0.20	0.604	1.804	4.20
0.500	1.500	0.240	2	0.25	0.740	1.740	3.83
0.120	2.880	0.110	3	0.04	0.230	2.990	10.80
0.270	2.730	0.235	3	0.09	0.505	2.960	11.12
0.360	2.640	0.304	3	0.12	0.664	2.940	11.60
0.420	2.580	0.346	3	0.14	0.766	2.926	9.70
0.540	2.460	0.425	3	0.18	0.965	2.885	7.24
0.690	2.310	0.510	3	0.23	1.200	2.820	6.44
0.870	2.130	0.592	3	0.29	1.462	2.722	4.23

Copolymerization in THF

The copolymerization was studied at 60 and 70°C for a total monomer concentration of 2 mol/L. The variations of the copolymerization rate under these conditions are reported in Fig. 8 These variations are linear and agree with Relation (15). In THF a competitive complexation of A by the comonomer and by the solvent takes place. For given values of A_0 and D_0, the concentration of the AD

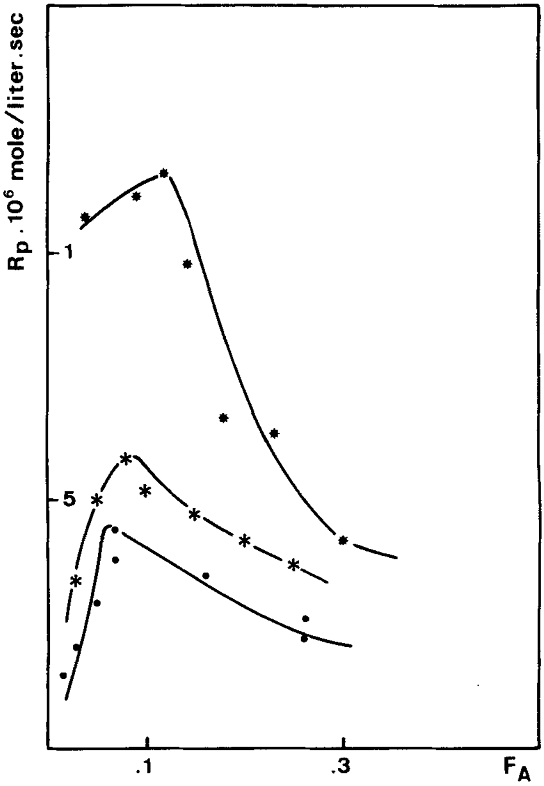

FIG. 6. Initial copolymerization rate vs the monomer feed molar ratio. [AIBN] = 10^{-2} mol/L. 60°C. Solvent: benzene. (•) M = 1.65 mol/L. (*) M = 2 mol/L. (∗) M = 3 mol/L.

complex decreases in THF (compared to the situation in benzene, and the participation of the AD complex becomes negligible).

Probabilities of Propagation by a Complex

We can define the probabilities P(C/X) of adding the complex for a growing chain terminated by X unit. These probabilities are given by [1e]

$$P(C/A) = \beta_1 K[A]/\beta_1 K[A] + 1 \qquad (16)$$

$$P(C/D) = \beta_2 K[D]/\beta_2 K[D] + 1 \qquad (17)$$

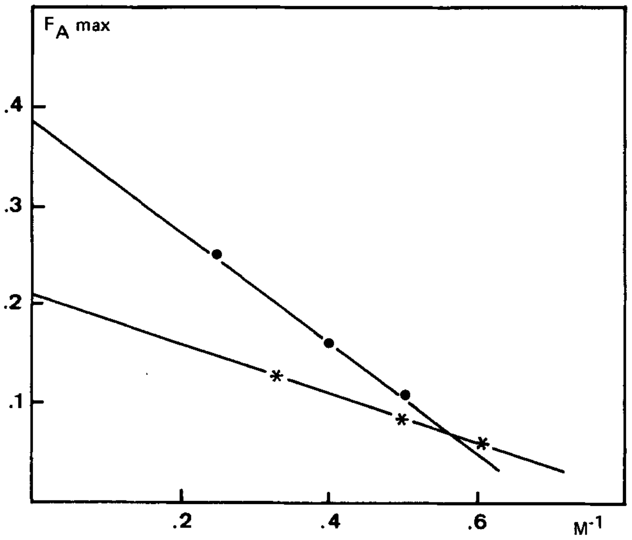

FIG. 7. Determination of the β_i values: variation of $F_{A_{max}}$ vs M^{-1}. (●): With [A] + [D] = M. (*): With $[A]_0 + [D]_0 = M_0$.

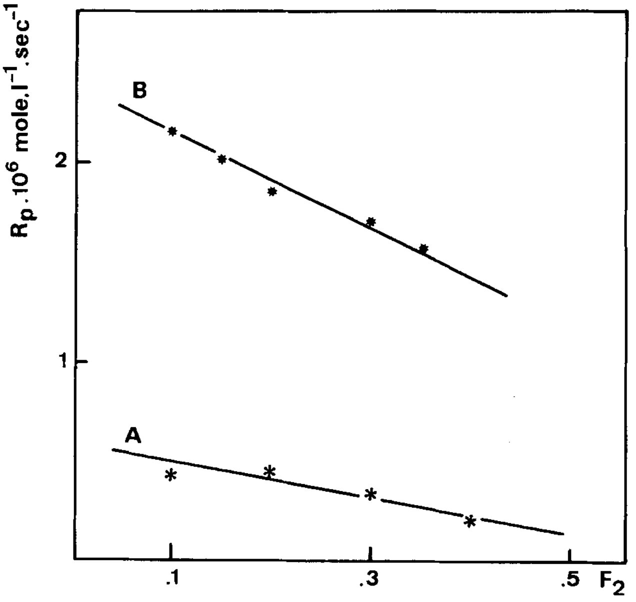

FIG. 8. Initial copolymerization rate vs the monomer feed ratio. [AIBN] = 10^{-2}/mol, M = 2 mol/L. Solvent: THF. (*) 60°C, (✱) 70°C.

The variation of Relations (16) and (17) under our experimental condition are reported in Figs. 9 and 10.

COMPARISON OF THE β_1 VALUES OBTAINED WHEN K IS OR IS NOT SMALL

If we suppose K to be small, we can write $[C] = KA_0D_0$, A_0 and D_0 being the initial concentrations of A and D. Then, using the same approximation described before, we obtain for the copolymerization rate [3]:

$$R_p = 2k_{AD}\left(\frac{R_i}{k_{to}}\right)^{0.5} [(1 - F_{A_0})M_0 + \beta_1 K(1 - F_{A_0})F_A M_0^2 + \beta_2 K(1 - F_{A_0})^2 M_0^2] \tag{18}$$

where $F_{A_0} = A_0/(A_0 + D_0)$ and $M_0 = A_0 + D_0$.

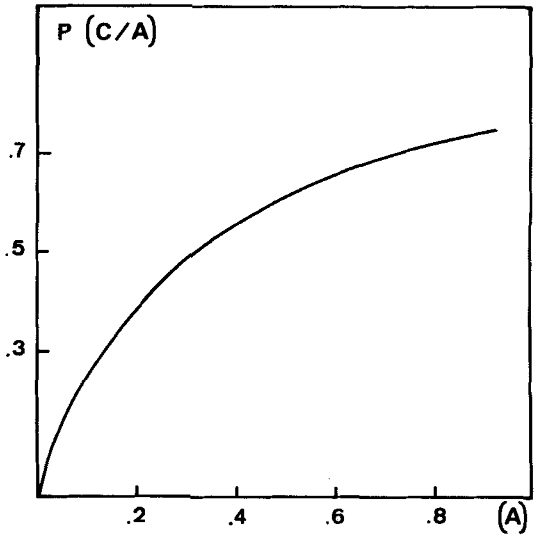

FIG. 9. Variation of the probability P(C/A) of adding an AD complex to a chain terminated by ~A° vs A concentration in the reactive medium.

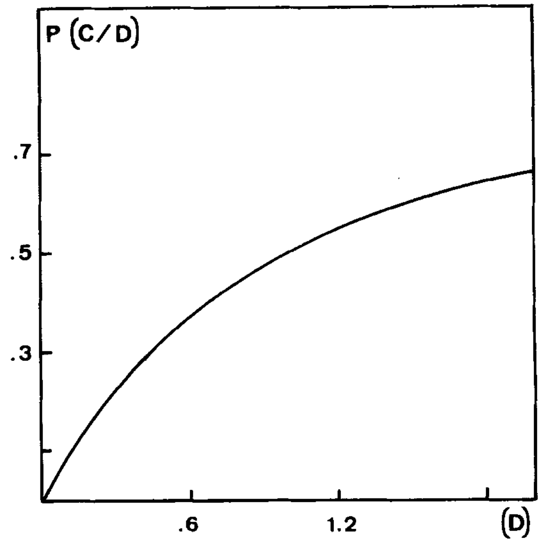

FIG. 10. Variation of the probability P(C/D) of adding an AD complex to a chain terminated by ~D° vs the D concentration in the reactive medium.

TABLE 4. Copolymerization of the AC/AV System at 60°C in Benzene at M_0 = Constant: Experimental Conditions and Rate of Copolymerization

	$R_p \times 10^6$ mol/L·s		
$F_{A_0} = A_0/(A_0+D_0)$	$M_0 = 2$ mol/L	$M_0 = 2.5$ mol/L	$M_0 = 4$ mol/L
0.05	2.22		
0.10	3.80	4.92	8.85
0.15		5.28	10.00
0.20	3.26		11.6
0.25		4.37	12.03
0.30	2.52	3.56	7.04
0.35	1.71		
0.50	0.98		

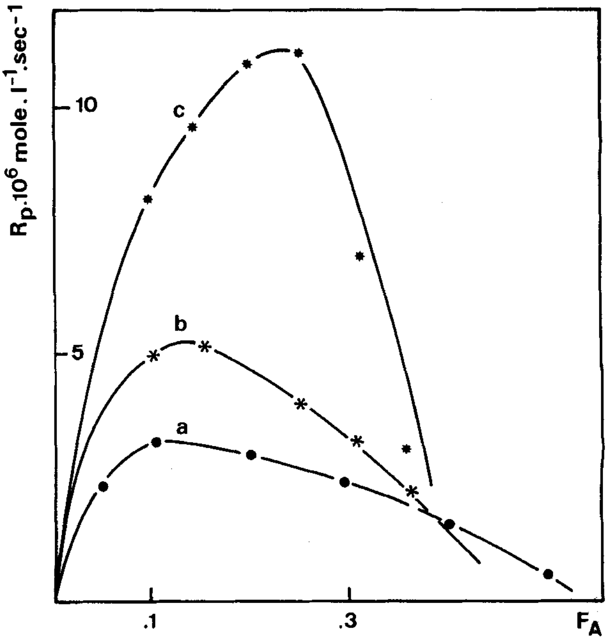

FIG. 11. Initial copolymerization rate vs the monomer feed ratio. [AIBN] = 10^{-2} mol/L. 60°C. Solvent: benzene. (●) M_0 = 2 mol/L. (*) M_0 = 2.5 mol/L. (*) M_0 = 4 mol/L.

In these conditions we obtain for the position of the maximum rate $(F_{A_0})_{max}$ the same equation as Eq. (12) with $M = M_0$. The experimental results for three values of M_0 are reported in Table 4 and Fig. 11. The copolymerization rates pass through a maximum vs F_{A_0}. Figure 7 reports the variation of $(F_{A_0})_{max}$ vs $1/M_0$. The linear relation yields $\beta_1 = 3.4$ and $\beta_2 = 0.6$.

The approximation $[C] = KA_0D_0$ produces an important error in the β_1 values.

CONCLUSION

We propose a new strategy to determine the values of the kinetic parameters of alternating copolymerization taking into account the participation of both monomers and a complex between them. Analysis of the experimental results is greatly simplified. We applied this method to the citraconic anhydride-vinyl acetate system. We showed that this copolymerization is an alternating one and that the two monomers form a charge transfer complex (K = 0.52 L/mol at 300 K). Kinetic analysis shows that the complex exhibits a greater reactivity than the monomers in the propagation reaction (about 10 and 4, respectively, in the case of vinyl acetate and citraconic anhydride).

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