Mechanism of Alternating Copolymerization of Vinyl Acetate and Maleic Anhydride

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ABSTRACT

Vinyl acetate and maleic anhydride are known to give 1:1 alternating copolymerization regardless of the monomer feed composition. The existence of a charge transfer complex between the comonomers has been shown and its equilibrium constant determined.
The mechanism has been discussed, starting from a study of the copolymerization rate when varying the solvent, the temperature, and the concentration of comonomers.

INTRODUCTION

The alternating copolymerization of maleic anhydride with various olefins using a free radical initiator has had much investigation (e.g., Refs. 1 to 6). Various mechanisms have been proposed in order to interpret the experimental results [3, 6, 7]. The current idea is that this type of polymerization involves the participation of a charge transfer complex between the comonomers. From this assumption two types of mechanism have been described in the literature.

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1. Homopolymerization of the charge transfer complex [6].
2. A mechanism involving the simultaneous participation of both free monomers and of the charge transfer complex [3, 7, 8].

The copolymerization of vinyl acetate and maleic anhydride yields alternating copolymers [1], and Mechanism 1 has been studied by Shantarovich and co-workers [2]. However, to date, the equilibrium constant of the charge transfer complex had not been determined and the velocity of the copolymerization had not been systematically studied. The aim of the present paper is to obtain detailed experimental data in order to test the Mechanism 1 and if necessary to suggest another type of interpretation.

EXPERIMENTAL

Materials

Vinyl acetate (VA) was purified according to a procedure described in the literature [9]. Maleic anhydride (MA), a commercial reagent, was twice recrystallized in purified chloroform, dried under reduced pressure, and then distilled under 10^{-1} Torr pressure just before use. 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 content was degassed, and they were sealed at the ends. The vessels were maintained during the time of the polymerization in a thermostat adjusted to $\pm 0.1°C$. The polymerization was stopped at low conversion, i.e., less than 10% at most, by a quick cooling of the polymerization vessel. The crude copolymers were precipitated in n-hexane and purified by successive dissolution in acetone and precipitation in n-hexane. Then the copolymers were dried under vacuum until constant weight was attained.

Characterization

Spectra

The UV spectra were recorded at 25°C from a Beckman D.B.G. spectrophotometer using 1 cm quartz cells. The ^{1}H NMR spectra were

obtained with a Varian A 60 spectrometer using T.M.S. as the internal reference and cyclohexane as solvent. IR spectra were recorded from films with a Perkin-Elmer 257 IR spectrophotometer. ^{13}C NMR spectra were recorded from hexadeuteroacetone solutions using a Jeol spectrometer.

Functional Analysis

The anhydride functions in the copolymeric chain were titrated at room temperature from solutions in a mixture of water and acetone by a conductimetric method [10] using a Wayne-Keer Autobalance Universal Bridge B 641.

RESULTS AND DISCUSSION

Charge Transfer Complex

The existence of a charge transfer complex between the comonomers was confirmed by the ^{1}H NMR spectra (Fig. 1). The chemical shift of the MA proton is affected by the addition of VA. The equilibrium
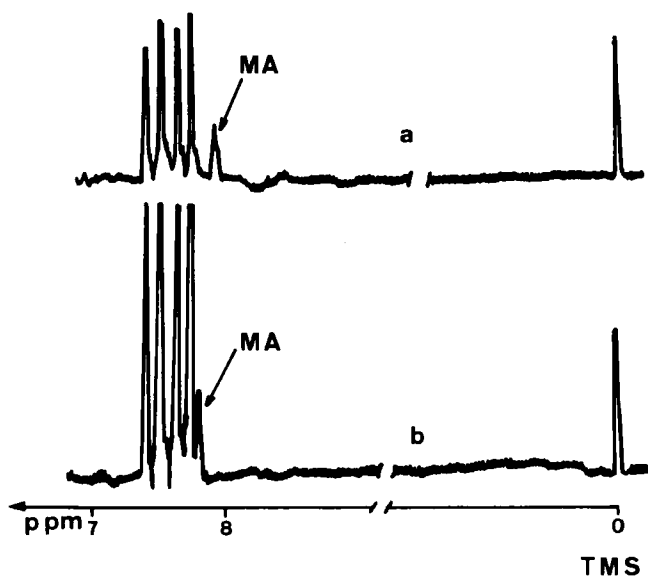

FIG. 1. Maleic anhydride (MA) proton chemical shifts (VA = vinyl acetate). Solvent, cyclohexane; reference, TMS. (a) [MA] = 10^{-2} mole/liter, [VA] = 2 moles/liter, (b) [MA] = 10^{-2} mole/liter, [VA] = 6 moles/liter.

constant in chloroform solution was determined by applying the
Benessi-Hildebrand method [11] to the optical density measurements
in the UV range.

We have the equilibrium

$$MA + VA \rightleftharpoons C$$

in which C refers to the charge transfer complex.

The equilibrium constant is defined as

$$K = [C]/[MA][VA]$$

At a given wavelength λ, the measured optical density D of a solution
is, with clear notations

$$D = \epsilon_C l[C] + \epsilon_{MA} l[MA]$$

If $[MA] \ll [VA]$, the following relationship can be written:

$$\frac{l[MA]_0}{D^*} = \frac{1}{\epsilon^*} (1 + \frac{1}{K[VA]})$$

with $[MA]_0$ = initial maleic anhydride concentration, $D^* = D - \epsilon_{MA}[MA]_0$,
and $\epsilon^* = \epsilon_C - \epsilon_{MA}$.

Figure 2 shows a plot of $l[MA]_0/D^*$ vs $1/[VA]$, and the numerical
results [12] are given in Table 1.

Electron donating solvents, especially benzene and acetone, give a
charge transfer complex with maleic anhydride. The equilibrium
constants of these complexations are 0.15 and 0.75 liter/mole,
respectively [4, 12]. Figure 3 shows the concentration of the MA/VA
complex in these two solvents vs the mole fraction of maleic anhydride
for different total concentrations of comonomers. We see that for the
MA/VA/acetone system the concentration of MA/VA complex is much
smaller than in the MA/VA/benzene system in the same conditions.

Copolymer Structure

The composition of copolymers, obtained by anhydride functional
group titration, always corresponds to the 1:1 composition within ex-
perimental error, irrespective of the widely varied monomer feed
ratios in the copolymerization experiments.

The structure of the copolymers was confirmed by IR and ^{13}C
NMR spectra. Figure 4 shows the IR spectrum of the copolymers.
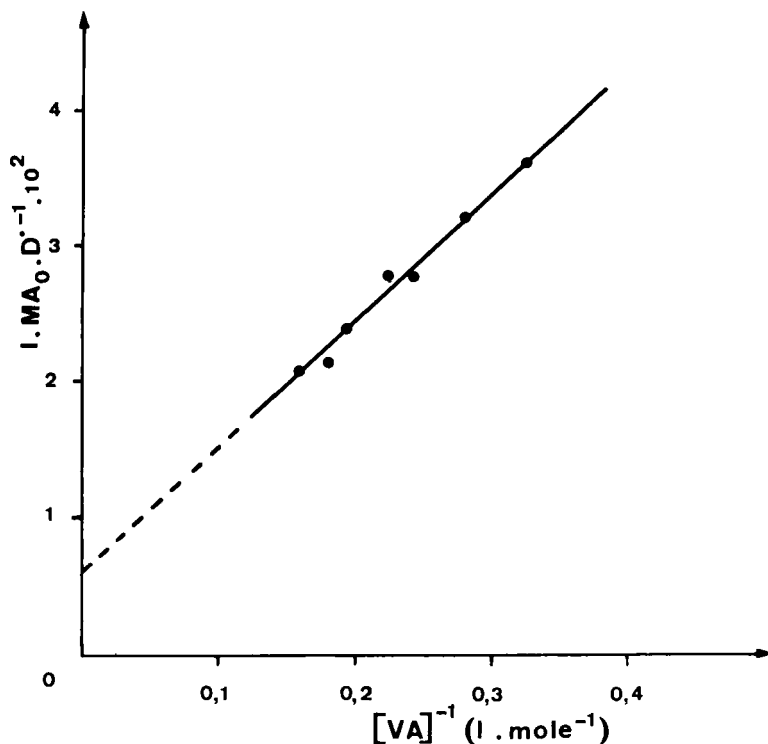This spectrum exhibits the characteristic IR absorption peaks at

FIG. 2. Benessi-Hildebrand plot. Temperature, 25°C; solvent, chloroform. $[MA] = 10^{-2}$ mole/liter, $3 < [VA] < 6$ moles/liter.

TABLE 1. K and ϵ Values of the VA/MA Complex

λ (nm)	ϵ (liter/(mole)(cm))	K (liter/mole)
270	150	0.06
275	217	0.06

1865 and 1785 cm^{-1} due to the anhydride ring and at 1745 cm^{-1} due to the ester functions. Figure 5 shows the ^{13}C NMR spectrum of the co-polymers. The spectrum is in good agreement with a 1:1 alternating structure. However, a very small peak at 132 ppm seems to be due to the presence of double bonds. These double bonds could originate from a thermal decomposition of the copolymer [13, 14].
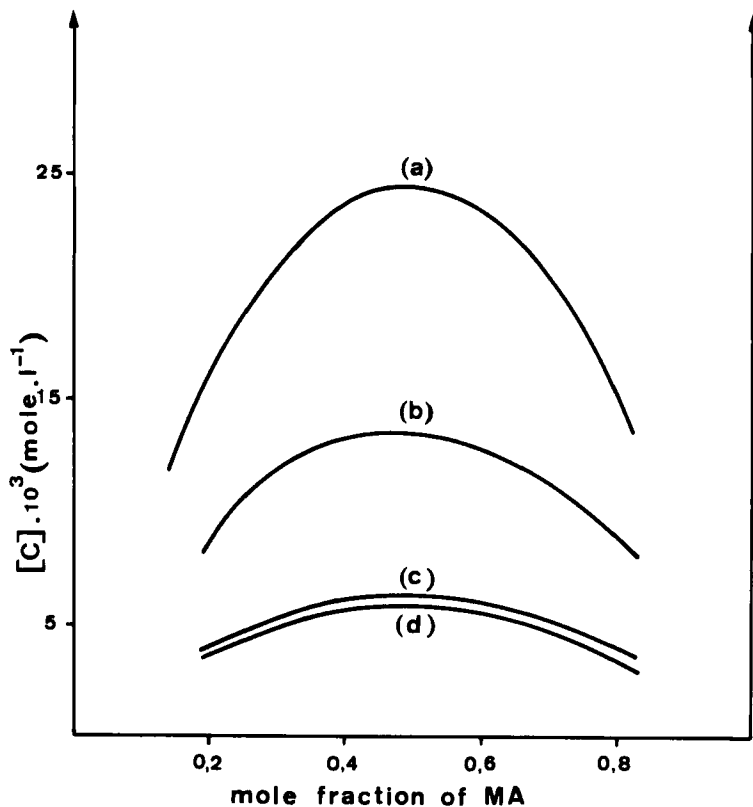
FIG. 3. Concentration of the MA/VA complex at 25°C. Solvent: benzene (a) 2 moles/liter, (b) 1.5 moles/liter, (d) 1 mole/liter, and acetone (c) 2 moles/liter.
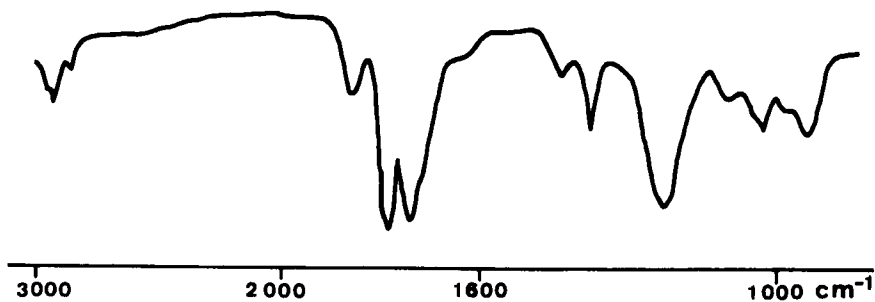

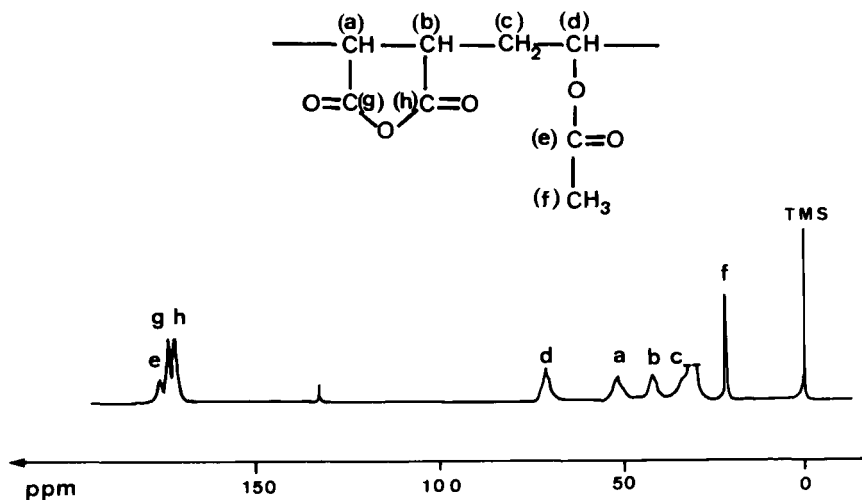FIG. 4. Infrared spectra of the MA-VA copolymers.

FIG. 5. ^{13}C NMR spectra of the MA-VA copolymers.

Rate Features

In benzene (Fig. 6) the dependence of the copolymerization rate R_p on the square root of the initiator concentration is linear. This dependence suggests the presence of a bimolecular termination. When the initial copolymerization rate is plotted against the monomer feed ratios, the maximum rate is found at a higher VA content in the feeding mixture of monomers. This maximum depends on the total concentration of comonomers. The results are shown in Table 2 and Fig. 7. In acetone, when the initial copolymerization rate at 60°C was plotted against the monomer feed ratios, the maximum rate was also found at a higher VA content in the feeding monomers mixture. On the contrary, when the copolymerization is carried out at 70°C, no maximum occurs and the copolymerization rate increases approximately linearly when the VA content in the feeding mixture of monomers is increased, as shown in Table 3 and Fig. 8.

Discussion of the Mechanism of Copolymerization

Shantarovich et al. [2] have proposed a mechanism in which the alternating copolymer is obtained by homopolymerization of the monomer charge transfer complex. Following this mechanism, the copolymerization
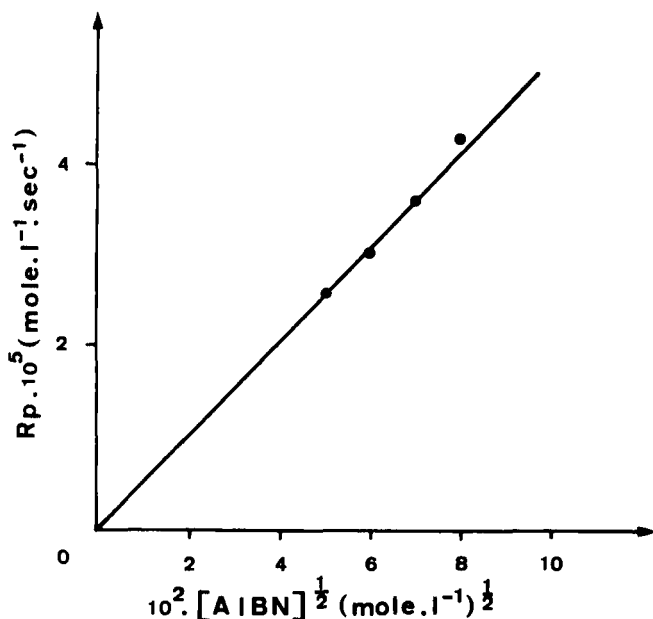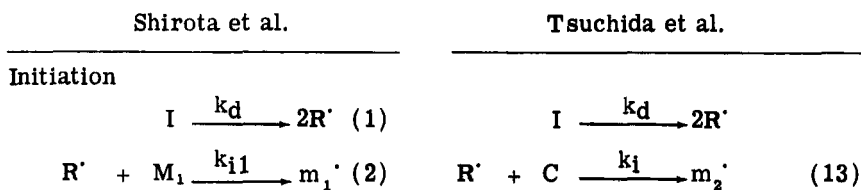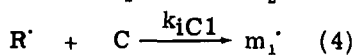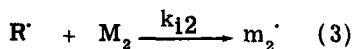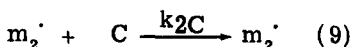
FIG. 6. Dependence of R_p on initiator concentration $[MA] = [VA] =$ 1 mole/liter. Solvent, benzene; temperature, 60°C.

rate should maximize at the monomer feed molar ratio of unity (1:1) for a fixed total monomer concentration. The rate features found in this work do not agree with this consequence of the above mechanism. The observation that the rate of the alternating radical copolymeriza-tion does not maximize at the monomer feed molar ratio of 1:1 has also been reported in the sytrene-maleic anhydride or chloro-2-ethyl vinyl ether-maleic anhydride systems by Tsuchida and his co-workers [3], and in the N-vinyl carbazole-fumaronitrile or N-vinyl carbazole-diethylfumarate systems by Shirota and his co-workers [7]. These two groups of authors proposed a mechanism to explain this type of copolymerization. These mechanisms are schematically described as following:

Shirota et al.	Tsuchida et al.

Initiation

$$I \xrightarrow{k_d} 2R^{\cdot} \quad (1) \qquad\qquad I \xrightarrow{k_d} 2R^{\cdot}$$

$$R^{\cdot} + M_1 \xrightarrow{k_{i1}} m_1^{\cdot} \quad (2) \qquad R^{\cdot} + C \xrightarrow{k_i} m_2^{\cdot} \qquad (13)$$

$$R^\cdot + M_2 \xrightarrow{k_{12}} m_2^\cdot \quad (3)$$

$$R^\cdot + C \xrightarrow{k_{iC1}} m_1^\cdot \quad (4)$$

$$R^\cdot + C \xrightarrow{k_{iC2}} m_2^\cdot \quad (5)$$

Propagation

$$m_1^\cdot + M_2 \xrightarrow{k_{12}} m_2^\cdot \quad (6) \qquad m_2^\cdot + C \xrightarrow{k_{2C}} m_2^\cdot \quad (14)$$

$$m_2^\cdot + M_1 \xrightarrow{k_{21}} m_1^\cdot \quad (7) \qquad m_2^\cdot + M_1 \xrightarrow{k_{21}} m_1^\cdot \quad (15)$$

$$m_1^\cdot + C \xrightarrow{k_{1C}} m_1^\cdot \quad (8) \qquad m_1^\cdot + C \xrightarrow{k_{1C2}} m_2^\cdot + M_1 \quad (16)$$

$$m_2^\cdot + C \xrightarrow{k_{2C}} m_2^\cdot \quad (9)$$

Termination

$$m_1^\cdot + m_1^\cdot \xrightarrow{k_{t11}} P \quad (10) \qquad m_1^\cdot + m_1^\cdot \xrightarrow{k_{t11}} P$$

$$m_1^\cdot + m_2^\cdot \xrightarrow{k_{t12}} P \quad (11) \qquad m_1^\cdot + m_2^\cdot \xrightarrow{k_{t12}} P$$

$$m_2^\cdot + m_2^\cdot \xrightarrow{k_{t22}} P \quad (12) \qquad m_2^\cdot + m_2^\cdot \xrightarrow{k_{t22}} P$$
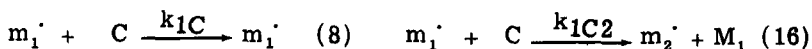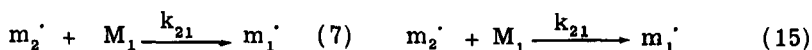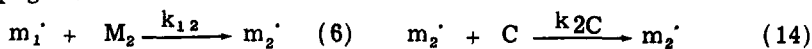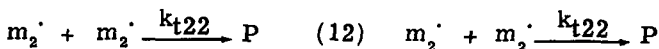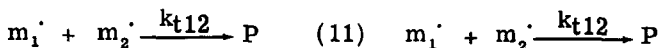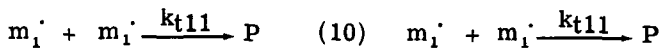
TABLE 2. Initial Copolymerization Rates (R_p) in Benzene[a]

MA mole fraction in the feeding mixture of monomers	$R_p \times 10^5$ [b] (mole/(liter)(sec)		
	A	B	C
0.1	4.15	3.90	3.05
0.2	5.20	5.00	3.57
0.3	5.85	5.25	2.85
0.4	6.00	3.95	2.37
0.5	3.65	2.2	0.65
0.6	0.3		

[a]Copolymers A were obtained under the following reactions conditions: $[AM] + [AV] = 2$ moles/liter; $[AIBN] = 5 \times 10^{-3}$ mole/liter; solvent, benzene; temperature, $60°C$. Copolymers B: $[AM] + [AV] = 1.5$ moles/liter. Copolymers C: $[AM] + [AV] = 1$ mole/liter. The other conditions for Copolymers B and C are the same as for copolymers A.

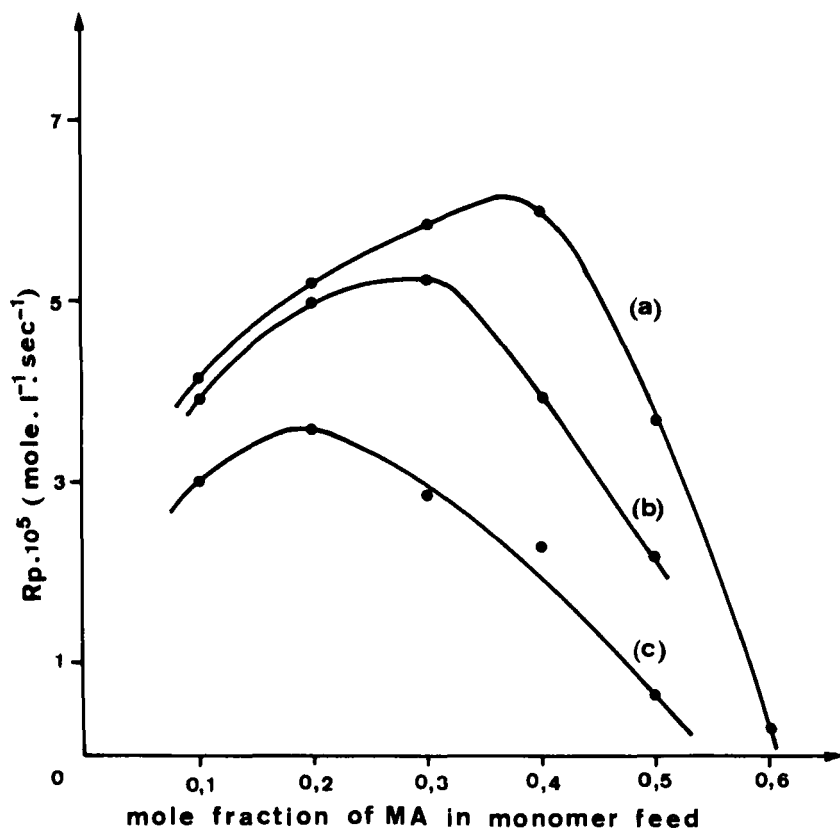[b]$R_p = d[P]/dt = -(1/2)(d/dt)([M_1] + [M_2])$.

FIG. 7. Initial copolymerization rates vs the monomer feed molar ratio $[AIBN] = 5 \times 10^{-3}$ mole/liter. Temperature, $60°C$; solvent, benzene. (a) $[AM] + [AV] = 2$ moles/liter. (b) $[AM] + [AV] = 1.5$ moles/liter. (c) $[AM] + [AV] = 1$ mole/liter.

Let us examine the particular case of the MA-VA copolymerization. M_1 and M_2 represent the free monomers (VA and MA, respectively), and C the charge transfer complex between them, and $m_1^{\cdot}$ and $m_2^{\cdot}$ refer to the growing chains corresponding to VA and MA radical ends. It is known that maleic anhydride can homopolymerize by a radical process [15], but in the classical conditions of copolymerization no homopolymer of MA can be obtained. In the conditions used for our copolymerization experiments it seems that the MA radical is much more stable than the

TABLE 3. Initial Copolymerization Rates (R_p) in Acetone[a]

Mole fraction of AM in monomer feed	$R_p \times 10^5$ (mole/(liter)(sec))	
	A	B
0.1	3.55	0.53
0.2	2.48	1.00
0.3		0.64
0.4	1.05	0.16
0.5	0.4	

[a]Reactions conditions for Copolymers A: [AIBN] = 5×10^{-3} mole/ liter; [AM] + [AV] = 2 moles/liter; temperature, 70°C; solvent, acetone. Copolymers B: temperature, 60°C; the other conditions are the same as for Copolymers A.
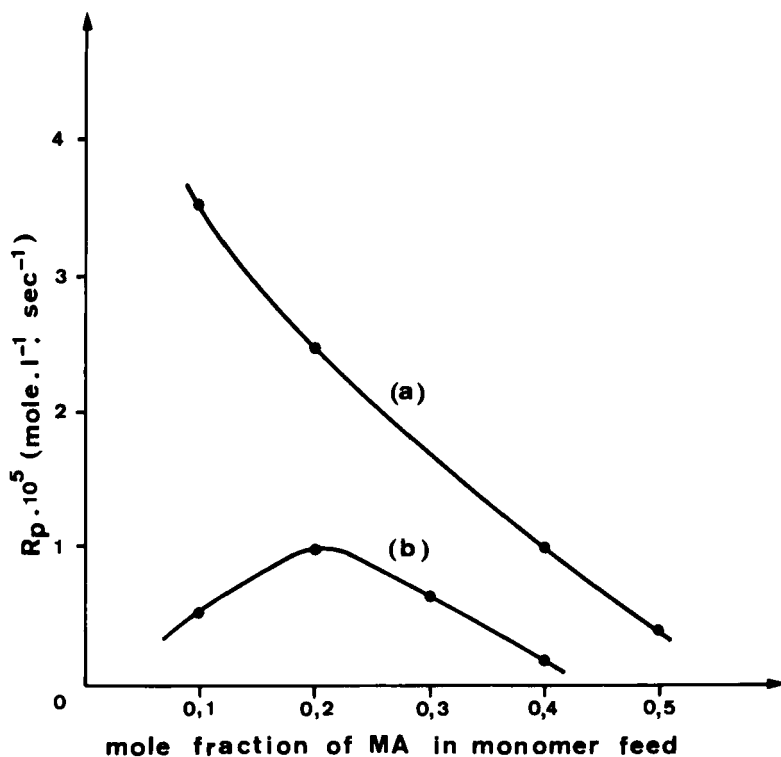
FIG. 8. Initial copolymerization rates vs the monomer feed molar ratio [AIBN] = 5×10^{-3} mole/liter [AM] + [AV] = 2 moles/liter. Solvent, acetone. Temperature, (a) 70°C and (b) 60°C.

VA radical. Thus the concentration of VA radicals should be smaller than the concentration of MA radicals, and the termination process should occur principally by reaction between two MA radicals. Since the equilibrium constant K for the formation of a charge transfer complex is very small, we have

$$[C] = K[M_1][M_2] \tag{17}$$

The overall copolymerization rate R_p is defined as

$$R_p = -(1/2)d/dt([M_1] + [M_2]) \tag{18}$$

Following this point of view, it is interesting to test the ability of the two preceeding models to explain our experimental results.

1. If we consider the Shirota et al. mechanism, we can definite two extreme cases. On the one hand, when the concentration of the charge transfer complex between the monomers is very low, then its reactions can be neglected. On the other hand, when the concentration of this complex is relatively high and its reactivity is very great, then the contribution of the free monomers can be negligible. By applying the steady-state approximation in these two cases, we obtain

$$R_p = \frac{k_{21}R_i^{1/2}}{(2k_{t22})^{1/2}}[M_1] \qquad ([C] \text{ very low}) \tag{19}$$

$$R_p \simeq \frac{k_{2C}R_i^{1/2}K}{(2k_{t22})^{1/2}}[M_1][M_2] \quad (\text{high values of } [C]) \tag{20}$$

where R_i is the rate of initiation.

In the intermediate case when the free monomers and the charge transfer complex are in competition in the different steps of the copolymerization, the copolymerization rate can be written as the sum of these two contributions:

$$R_p = A[M_1] + B[M_1][M_2] \tag{21}$$

where

$$A = \frac{k_{21}R_i^{1/2}}{(2k_{t22})^{1/2}}; \qquad B = \frac{k_{2C}KR_i^{1/2}}{(2k_{t22})^{1/2}}$$

Let us call $[M_1] + [M_2] = [T]$. If F_2 is the mole fraction of M_2:

$[M_1] = (1 - F_2)[T]$

$[M_2] = F_2[T]$

and Eq. (21) becomes

$$R_p = (1 - F_2)[T](A + BF_2[T])$$ (22)

The maximum of R_p is obtained for

$$\frac{\partial R_p}{\partial F_2} = 0 \quad \text{and} \quad F_{2\,max} = \frac{1}{2} - \frac{A}{2B}\frac{1}{[T]}$$ (23)

We should have a linear relation between the mole fraction of M_2 in the monomer feed and the inverse of the total concentration of comonomers.

In the case of our MA/VA copolymerization experiments in benzene, the concentration of the charge transfer complex between the monomers is relatively high and Relation (23) is verified (Fig. 9).

For the copolymerization experiments in acetone, the influence of temperature is very important. At $60°C$ there is a competition between free monomers and the charge transfer complex. A maximum of the copolymerization rate appears for $F_2 = 0.21$, while at $70°C$ no maximum is observed. Due to the fact that the reaction of formation of a charge transfer complex is an exothermic one [4, 12], the concentration of the charge transfer complex is smaller at $70°C$ than at $60°C$. Because the influence of the complex is negligible at $70°C$, under these conditions we obtain a linear relationship between the copolymerization rate and the VA mole fraction in the monomer feed (Fig. 8), in good agreement with Relation (19).

It can be seen that our experimental results are compatible with the mechanism assumed by Shirota and his co-workers.

2. Let us now consider the Tsuchida et al. mechanism. With the same notations as above, we obtain for the copolymerization rate

$$R_p = (1 - F_2)[T](A + BF_2[T])$$ (24)

where

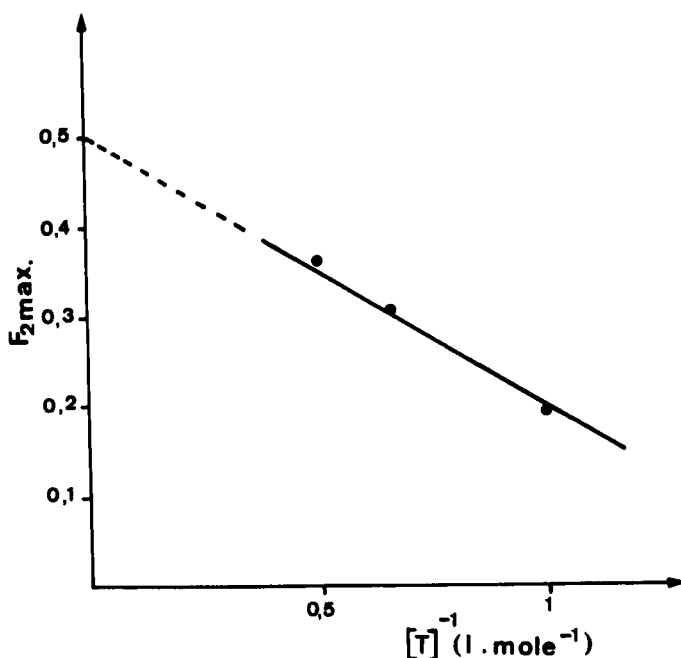$$A = \frac{R_i^{1/2}k_{21}}{(2k_{t22})^{1/2}} \qquad B = \frac{R_i^{1/2}k_{2C}K}{(2k_{t22})^{1/2}}$$

FIG. 9. Relation between $F_{2\,max}$ and the inverse of the total con-
centration of comonomers. Solvent, benzene; [AIBN] = 5×10^{-3} mole/
liter; temperature, 60°C.

Due to the fact that the mathematical form of Relation (24) is the same
as that of Relation (22), the same conclusions as in the Shirota et al.
model can be deduced. The maximum copolymerization rate in benzene
is defined by Eq. (23), and in acetone at 70°C, when the charge transfer
complex concentration is very low, a linear relation between the rate
and the VA mole fraction in the monomer feed is also obtained.

Thus our experimental results are also compatible with the
mechanism suggested by Tsuchida et al.

From a kinetic point of view it is very hard to make a choice between
these two mechanisms which differ essentially in the role played by
the charge transfer complex in the propagation reactions. For Shirota,
the complex behaves as a monomer. For Tsuchida, when the addition
of the complex occurs on a growing chain bearing a VA radical end, a
molecule of monomeric VA is rejected (Eq. 16).

Knowledge of the structure of the charge transfer complex between

the monomers would be very interesting for predicting its reactivity. Unfortunately, this problem is rather difficult because it is impossible to isolate the complex.

ACKNOWLEDGMENTS

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