Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Studies in Cyclocopolymerization. IX. A Systematic Kinetic Study on the Cyclocopolymerization of Vinyl Ethers with Maleic Anhydride in Different Solvents

Bruno Zeegers[a]; George B. Butler[a]
[a] Department of Chemistry, University of Florida, Gainesville, Florida

To cite this Article Zeegers, Bruno and Butler, George B.(1972) 'Studies in Cyclocopolymerization. IX. A Systematic Kinetic Study on the Cyclocopolymerization of Vinyl Ethers with Maleic Anhydride in Different Solvents', Journal of Macromolecular Science, Part A, 6: 8, 1569 — 1608

To link to this Article: DOI: 10.1080/10601327208056915

URL: http://dx.doi.org/10.1080/10601327208056915

J. MACROMOL. SCI.—CHEM., A6(8), pp. 1569-1608 (1972)

Studies in Cyclocopolymerization. IX. A Systematic Kinetic Study on the Cyclocopolymerization of Vinyl Ethers with Maleic Anhydride in Different Solvents

BRUNO ZEEGERS and GEORGE B. BUTLER

Department of Chemistry
University of Florida
Gainesville, Florida 32601

ABSTRACT

The kinetics of the AIBN-initiated copolymerization of divinyl ether (DVE) and ethyl vinyl ether (EVE) with maleic anhydride (MA) was extensively studied in seven different solvents. The yield at 100% conversion as a function of the feed composition when the total monomer concentration is kept constant gave a confirmation of the composition of these copolymers: DVE/MA = 1/2 and EVE/MA = 1/1. The study of the initial rate as a function of the feed composition made it possible to determine the relative values of the different propagation rate constants consistent with a mechanism by successive and selective additions: in the EVE-MA system, the addition of EVE is slower than the addition of MA; in the DVE-MA system, the addition of

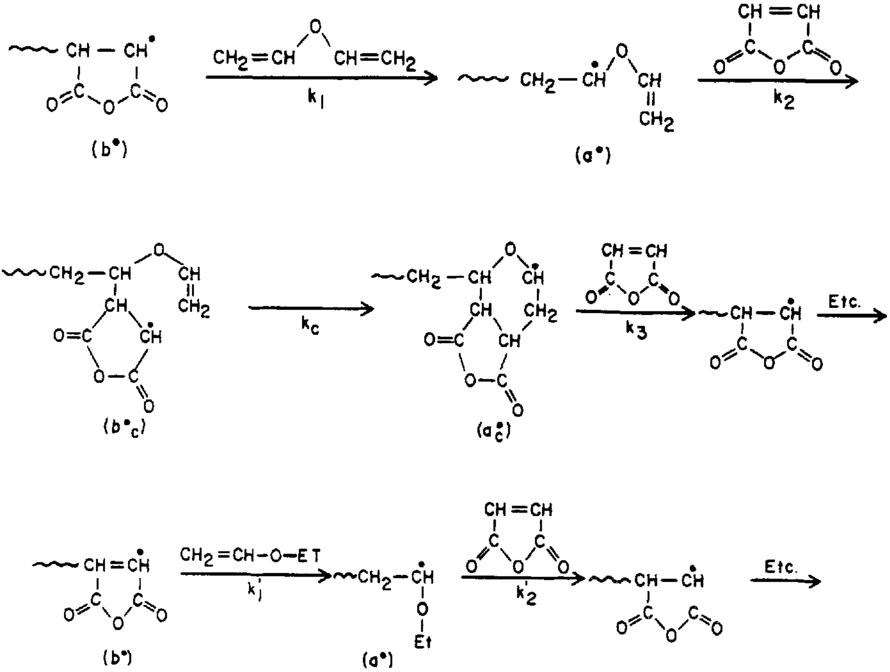
DVE is slower than the addition of the first MA molecule, while the addition of the second MA molecule is slower than the first one. The study of the dependence of the monomer concentration, of the AIBN concentration, and of the efficiency of the initiator, on the rate of polymerization, shows finally that the true order of the monomer concentration is close to 1 while its apparent order varies from 1 to 2. From all the kinetic data it was observed that the mechanism of these copolymerizations can be explained without relying upon the concept of participation of the charge-transfer complex formed between the monomers. However, participation of the complex in a competing mechanism with the above cannot be completely excluded.

INTRODUCTION

The copolymerization of divinyl ether (DVE) with maleic anhydride (MA) is a very interesting system from the point of view of a kinetic study because practically no homopolymerization occurs when initiated by a radical initiator. In any conditions the composition of the copolymer remains constant: DVE/MA = 1/2. This kind of copolymerization has already been extensively studied [1-4]. It was shown that the monomers form a charge-transfer complex and several experiments previously led to the postulate of participation of the complex in the mechanism of polymerization, suggesting homopolymerization of a complex. However, all the facts leading to that conclusion were not absolute, and no definitive experiment supporting this concept was given; it was the reason of looking further and doing additional and systematic experiments in different solvents.

The mechanism of the DVE-MA copolymerization was proposed earlier (see below): three steps are involved (four steps if the cyclization is included); therefore, the kinetic study is in fact complicated, and it was decided to study also the copolymerization of ethyl vinyl ether (EVE) with MA because this system is similar to the DVE-MA system but offers a simpler kinetic treatment: indeed, two steps are involved.

The elementary mechanism of DVE-MA and EVE-MA copolymerizations can be expressed as



EXPERIMENTAL

DVE and EVE were distilled at 28-29 and 34-35°C, respectively. MA was sublimated in vacuo (mp 54°C). AIBN was recrystallized from methanol. Reagent or spectrograde solvents were used. The UV study was carried out with a Beckman DK-2A Spectrophotometer at 23°C in a cell of 1 cm. When one component of the complex absorbs in the same region as the region of absorption of the complex, the reference cell was filled with that component at the same concentration as in the complex solution cell or the absorption of the pure component was deducted from the optical density measured in order to determine the exact value of the optical density of the complex. IR spectra were recorded on a Perkin-Elmer Spectrophotometer (Infracord). Molecular weights were determined by a vapor pressure osmometer, Mechrolab Model 302. Compositions of the copolymers were determined by titration of MA units with a high frequency oscillometer, Sargent Chemical Oscillometer, Model V. Elemental analyses were carried out by Atlantic Microlab, Inc.

The polymerizations were carried out in thick glass tubes of 5, 10, or 20 ml under high vacuum (10^{-5} Torr) after two successive degasifications. The temperature of polymerization was kept constant at 60°C with a large oil bath. The polymeric solutions were precipitated by boiling diethyl ether, filtered, and washed extensively with boiling ether, and finally the polymers were dried at approximately 50°C in vacuo. The rates of polymerization were determined by gravimetry.

Study of the Complexes

The study of the complexes between vinyl ethers and different electron acceptors has already been presented in several previous papers [3-5]. It was observed that the complexes always showed 1:1 stoichiometry and that their equilibrium constants are very small. In the present paper the previous study was completed in the solvents employed in the polymerization study. Similar results were obtained: DVE-MA and EVE-MA complexes show 1:1 stoichiometry in all solvents as determined by the continuous variation method [6] (Figs. 1 and 2); in acetonitrile, the equilibrium constant of the DVE-MA complex, determined by the Benesi-Hildebrand relation [7], is so low that it was not possible to evaluate its value accurately: $K < 0.08$ (the molar extinction coefficient is greater than 500 at 290 mμ) (Fig. 3).

In acetophenone, UV measurements were not possible due to the strong absorption of the solvent. Moreover, on account of the fact that both acetophenone and benzonitrile show some electron-acceptor character, it was postulated that these solvents might form complexes with DVE and EVE. In fact, no enhancement of the optical density was observed even when pure DVE or EVE was mixed with these solvents.

A strong complex between MA and toluene did not permit the study of DVE-MA and the EVE-MA complexes in toluene. The complex toluene-MA showed a 1:1 stoichiometry (Fig. 4); the molar extinction coefficient is equal to 0.5 at 360 mμ and the equilibrium constant is equal to 1.37 (Fig. 5). This high value indicates that 93% of MA is complexed when MA at 1 mole/liter is dissolved in pure toluene (9.4 moles/liter). Equilibrium constants of the same order of magnitude were described by Barb [8] for MA-aromatic complexes.

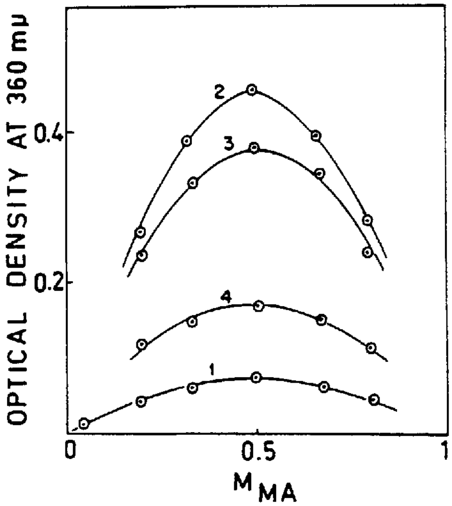


FIG. 1. Determination of the stoichiometry of the DVE-MA complex in acetone (1), in methylene chloride (2), in acetonitrile (3), and in benzonitrile (4). In (1): (DVE) + (MA) = 1 mole/liter; in (2), (3), and (4): (DVE) + (MA) = 0.8 mole/liter.

The Yield as a Function of the Feed Composition

It was of considerable interest to measure the yield of polymer obtained for different feed compositions and after different times of polymerization when the total monomer concentration was kept constant.

When the time of polymerization was long enough so that the rate of polymerization becomes very slow, it was observed that the yield for different feed compositions corresponded exactly to the theoretical maximum of conversion of a perfect 1:1 copolymer for the EVE-MA system (Figs. 6-12) or a perfect 1:2 copolymer for the DVE-MA system (Figs. 13-19). These facts lend excellent support to the values of the composition of the polymers determined by titration of the maleic anhydride units. However, in dimethyl formamide (DMF), both EVA-MA and DVE-MA copolymerizations are so slow that a maximum of 15% conversion was observed, even after 24 hr, for MA molar fraction in the feed equal to 0.1-0.2.

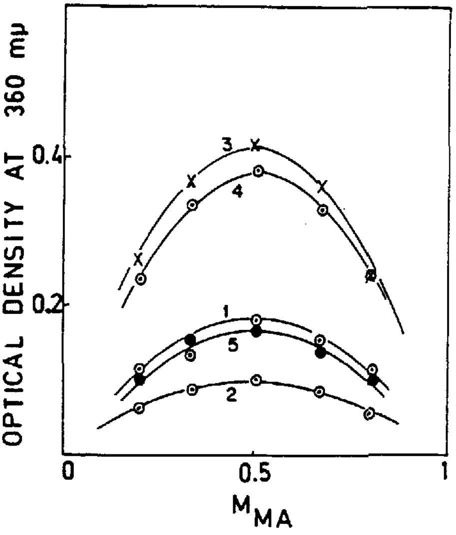


FIG. 2. Determination of the stoichiometry of the EVE-MA complex in dimethyl-formamide (1), in acetone (2), in methylene chloride (3), in benzonitrile (4), and in acetonitrile (5). (DVE) + (FN) = 1 mole/liter.

As expiained below, the study of the initial yield (or initial rate) as a function of the feed composition when the total monomer concentration is kept constant will give information on the role of the charge-transfer complex in the mechanism of polymerization. The facts that the copolymers always show constant compositions and that the rate of copolymerization is extremely fast compared to the rate of homopolymerization of the monomers suggest strongly the existence of specific interactions. Two theories are generally developed. The first [3, 4] assumes that the specific interaction occurs between the monomers; a complex is formed with a reactivity higher than the monomers; the polymerization is considered as homopolymerization of the complex, and an alternating copolymer is formed. The other [9] involves specific interactions between a growing radical and the monomer of different polarity leading also to alternate polymerization; even if a complex formation is not excluded (a complex is

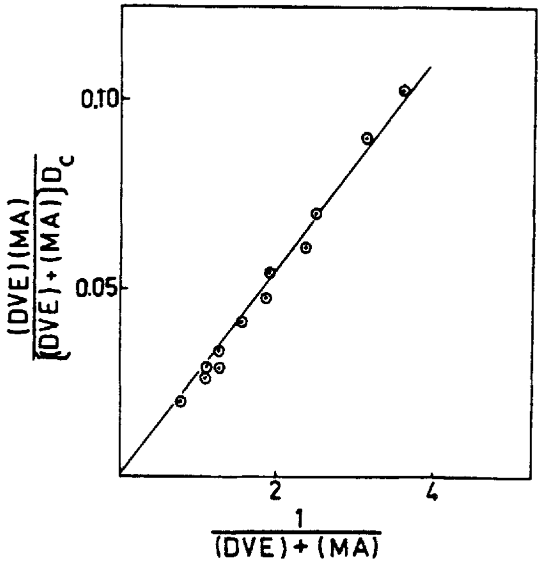


FIG. 3. Determination of the equilibrium constant of the DVE-MA complex in acetonitrile. The optical density of the complex, D_c, was measured at 290 mμ. (MA) = 0.05 or 0.025 mole/liter.

evidently expected between monomers of different polarity...), its direct participation in the mechanism is considered to be open to question.

The study presented in this paper will, perhaps, contribute to some extent to the solution of this crucial problem. It is observed from Figs. 6-19 that the feed composition for which the initial rate is maximum when the total concentration is kept constant does not generally correspond to the composition of the polymers. As described further, this important conclusion would support preferentially a mechanism by successive and selective additions of monomers rather than by complex participation.

Consider the results of the EVE-MA system, and suppose first that the copolymerization is only due to the homopolymerization of the EVE-MA complex. The rate of polymerization can be expressed by

$$\text{rate} = kcr \qquad (1)$$

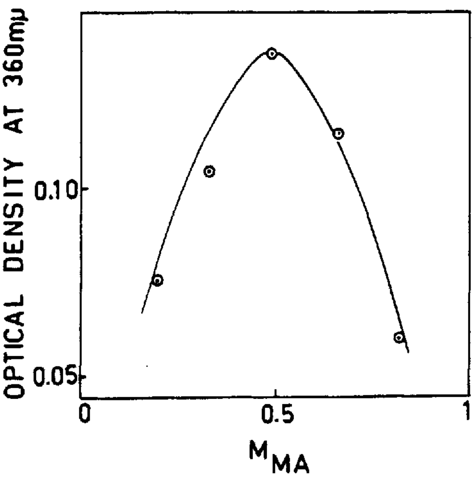


FIG. 4. Determination of the stoichiometry of the complex formed between toluene and MA in methylene chloride. (Toluene) + (MA) = 1 mole/liter.

where c is the concentration of complex and r the concentration of growing radicals. The concentration of complex is related to the concentration of EVE and MA (represented by a and b) by the equilibrium constant K (for a 1:1 complex)

$$K = \frac{c}{(a - c)(b - c)} \tag{2}$$

For constant total monomer concentration, a + b = constant, but for different molar fractions of EVE and MA (M_a and M_b), c takes a maximum value when a = b, or $M_a = M_b = 0.5$.

The concentration, r, of growing radicals depends on the concentration of radicals initiating the polymerization per unit time multiplied by the mean lifetime of the radicals. If the variations of initial rate (for variations of M_a and M_b) are only due to variations of r, then there must be variations either of the concentration of the radicals initiating the polymerization or of the mean

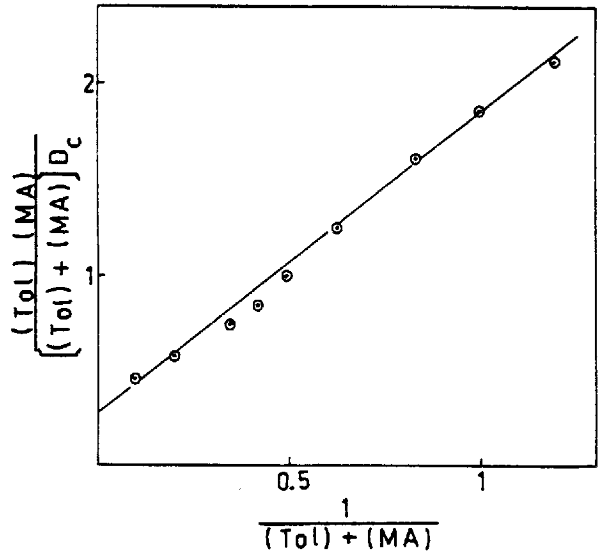


FIG. 5. Determination of the equilibrium constant of the complex toluene-MA in methylene chloride. (MA) = 0.4 mole/liter. The optical density, D_c, was measured at 360 mμ.

lifetime of the radicals. If variations in the rate are due only to variations of the concentration of radicals initiating the polymerization, it would be expected that the nitrogen percentage of the polymers (the nitrogen percentage being a direct measurement of the number of butyronitrile radicals initiating the polymerization) should be constant since for each initiating radical, a constant number of monomers would be added. However, the data shown in Fig. 20 indicate that the percentage of nitrogen generally decreases when the rate increases. Therefore, variations of the rate cannot be due only to variations of the number of initiating radicals. In the present study, however, there is no absolute indication of the possible influence of the lifetime of the radicals on the rate of polymerization. There is only a presumption that this influence is negligible by considering the polymerization in acetophenone: in the EVE-MA system, the maximum of the rate is observed in the EVE-rich portion (Fig. 7), while in DVE-MA it is in the MA-rich portion (Fig. 14). If the rate depends only

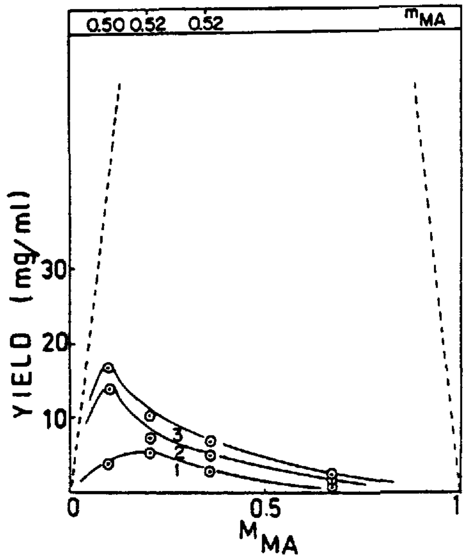


FIG. 6. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6×10^{-3} mole/liter. EVE-MA system in dimethyl formamide. 1: 145 min; 2: 645 min; 3: 900 min.

on the lifetime of the radicals, this would mean that the lifetime of radicals is higher for lower MA molar fraction in the EVE-MA system, but for higher MA molar fraction in the DVE-MA system. Such phenomena are not highly probable. However, as will be shown later, available evidence indicates some chain transfer occurs in these systems.

Therefore, on the basis of these considerations, it can be assumed that the concentration, r, of growing radicals is constant. According to expression (1), the rate would only depend on the concentration, c, of complex; and from relation (2), the initial rate when a + b = constant, would take a maximum value when a = b, or $M_a = M_b = 0.5$

It is observed from Figs. 3-10 that in every solvent the maximum

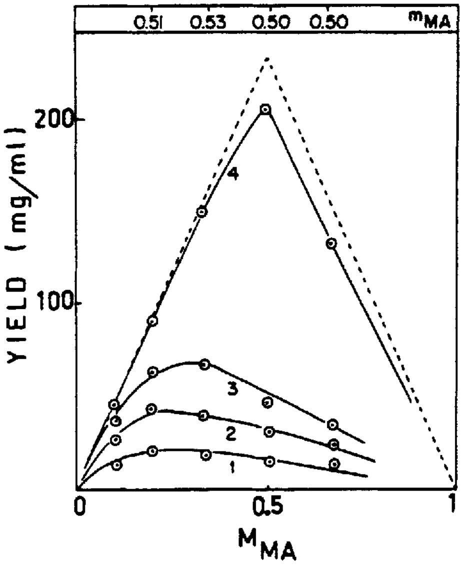


FIG. 7. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6 × 10^{-3} mole/liter. EVE-MA system in acetophenone. 1: 12.5 min; 2: 20 min; 3: 30 min; 4: 360 min.

of the initial rate was found in the EVE-rich portion, i.e., when a > b. For this reason it becomes difficult to explain the mechanism of polymerization by only the participation of the charge-transfer complex as the reactive specie. A similar conclusion was also drawn when it was observed that the dependence of total monomer concentration on the initial rate could be explained without the consideration of a complex in the mechanism. It is therefore reasonable that the copolymerization of EVE-MA, and the similar copolymerization of DVE-MA, follows preferentially a mechanism of successive and selective additions of monomers on radicals of different polarity. However, the present study does not permit the total exclusion of participation of a complex in addition to the mechanism by which simple monomer additions occur.

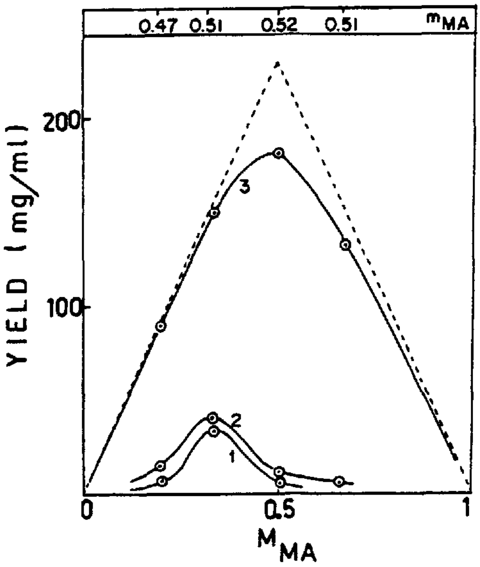


FIG. 8. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6×10^{-3} mole/liter. EVE-MA system in acetone. 1: 25 min; 2: 30 min; 3: 320 min.

If one considers only a mechanism by selective additions, the location of the molar fraction for which the initial rate is maximum permits the evaluation of the ratio of the rate constants of the two steps of the EVE-MA copolymerization. If a, b, a·, and b·, represent, respectively, the concentration of EVE, MA, EVE·, MA·, and k_1' and k_2' the rate constants of addition of EVE and MA, the rate is expressed by

$$\text{rate} = k_1'ab\cdot + k_2'ba\cdot \tag{3}$$

Since the composition of the copolymer is 1:1, the rates of addition of EVE and MA are equal (stationary conditions):

$$k_1'ab\cdot = k_2'ba\cdot \tag{4}$$

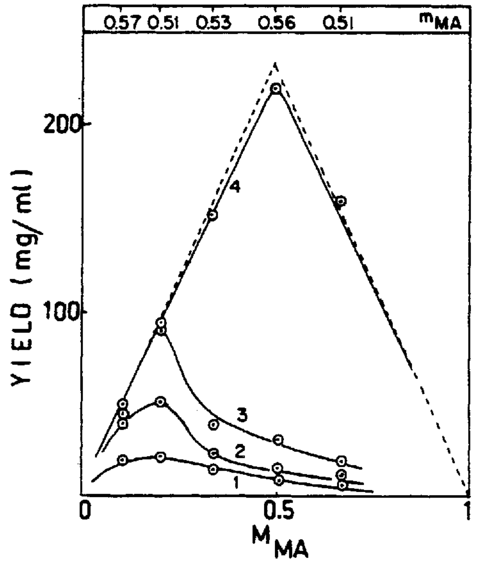


FIG. 9. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6 × 10^{-3} mole/liter. EVE-MA system in methylene chloride. 1: 6.5 min; 2: 8 min; 3: 10 min; 4: 360 min.

If r is the total concentration of growing radicals ($r = a^{\cdot} + b^{\cdot}$), the following expression is obtained:

$$\text{rate} = 2r\frac{k_1'k_2'ab}{k_1'a + k_2'b} \tag{5}$$

When a + b = m = constant, the maximum of the rate for variations of M_a ($M_a = a/m$; $M_b = b/m$) occurs when

$$d\ \text{rate}/da = 0 \tag{6}$$

It was shown that r is constant with the molar fractions of the

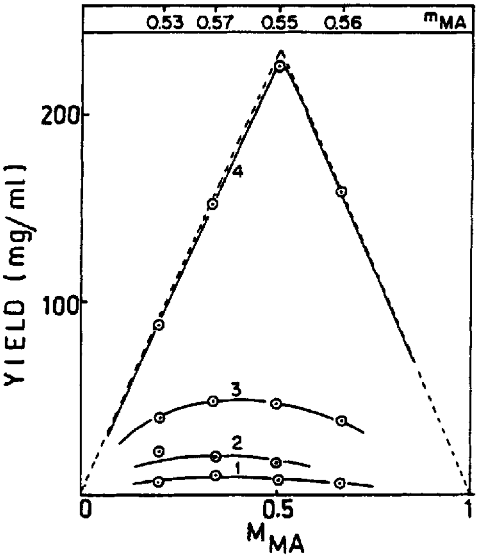


FIG. 10. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6 × 10^{-3} mole/liter. EVE-MA system in benzonitrile. 1: 10 min; 2: 12 min; 3: 15 min; 4: 80 min.

components; therefore, the derivative of expression (5) for variations of a is

$$\frac{d\ \text{rate}}{da} = (m - a)^2 - a^2\frac{k_1'}{k_2'} \tag{7}$$

The maximum initial rate occurs when

$$\left(\frac{m - a}{a}\right)^2 = \frac{k_1'}{k_2'} \tag{8}$$

or when

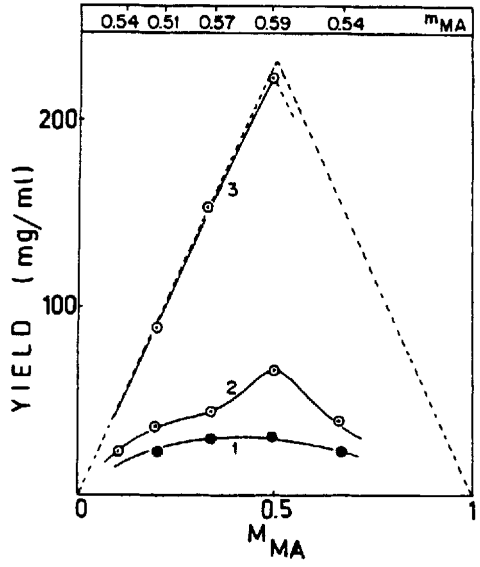


FIG. 11. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6 × 10^{-3} mole/liter. EVE-MA system in toluene. 1: 12 min; 2: 14 min; 3: 160 min.

$$\left(\frac{1 - M_a}{M_a}\right)^2 = \frac{k_1'}{k_2'} \tag{9}$$

M_a in relation (9) represents the value of the molar fraction of a for which the rate is maximum; since M_a is determined experimentally, it therefore becomes possible to evaluate the ratio k_1'/k_2'. The values are recorded in Table 1.

The addition of EVE is a slower process than the addition of MA; it can be understood that the radical of MA is a stable radical, i.e., less reactive, so that the addition of EVE becomes a relatively slow process. It was also observed that in toluene k_2' is comparatively smaller than k_1' than in the other solvents. It is quite

TABLE 1. Molar Fraction of Ether in the Feed, for Which the Initial Rate is Maximum, and Relative Values of the Different Rate Constants

	EVE-MA system				DVE-MA system				
			Relative value				Relative value		
Solvent	M_a	k_1'/k_2'	k_1'	k_2'	M_a	k_1/k_3	k_1	k_2	k_3
Dimethyl formamide	0.9	0.012	1	81	0.85	0.019	1	81	52
Acetophenone	0.8	0.066	1	16	0.33	3.94	1	16	0.24
Acetone	0.7	0.18	1	5.5	0.55	0.49	1	5.5	2.04
Methylene chloride	0.85	0.031	1	32	0.50	0.97	1	32	1.03
Benzonitrile	0.65	0.28	1	3.5	0.33	3.72	1	3.5	0.26
Toluene	0.55	0.67	1	1.5	0.50	0.33	1	1.5	3.00
Acetonitrile	0.85	0.031	1	32	0.55	0.64	1	32	1.56

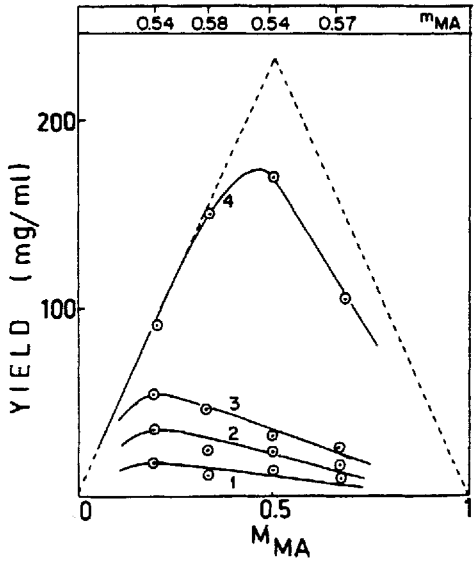


FIG. 12. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6 × 10^{-3} mole/liter. EVE-MA system in acetonitrile. 1: 20 min; 2: 28 min; 3: 35 min; 4: 660 min.

possible that the strong complexation of MA with toluene prevents the addition of MA to some extent.

The DVE-MA copolymerization probably follows a mechanism similar to the EVE-MA copolymerization. Similar expressions can be derived. If a, b, a·, b·, and a_c·, respectively represent the concentration of DVE, MA, DVE·, MA·, and cyclic radicals (see mechanism in the Introduction), and if k_1, k_2, and k_3 represent the rate constants of addition of DVE, and of the first and the second MA molecules, the rate expression becomes

$$\text{rate} = k_1 ab\cdot + k_2 ba\cdot + k_3 b a_c\cdot \qquad (10)$$

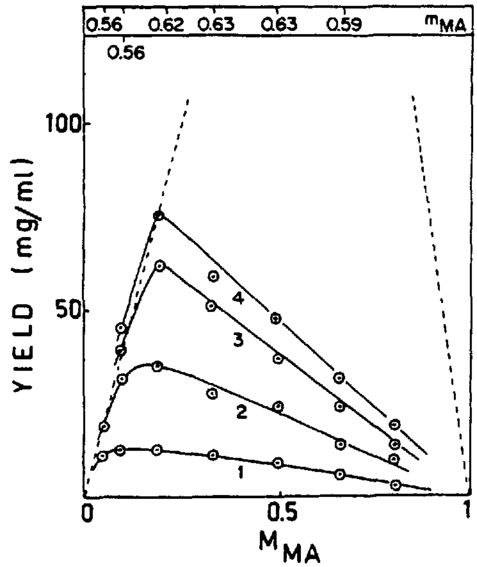


FIG. 13. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6 × 10^{-3} mole/liter. DVE-MA system in dimethyl formamide. 1: 120 min; 2: 300 min; 3: 720 min; 4: 1440 min.

The total concentration of radical, r, equals $a^{\cdot} + b^{\cdot} + a_c^{\cdot}$; the concentration of the radical just before the cyclization ($b_c^{\cdot}$) can be neglected since it is generally assumed that the cyclization step is a very fast process. In the same manner as in the EVE-MA system, one obtains

$$\text{rate} = 3r \frac{k_1 k_2 k_3 ab}{k_1 k_2 a + k_1 k_3 a + k_2 k_3 b} \tag{11}$$

For a + b = m = constant, the derivative is

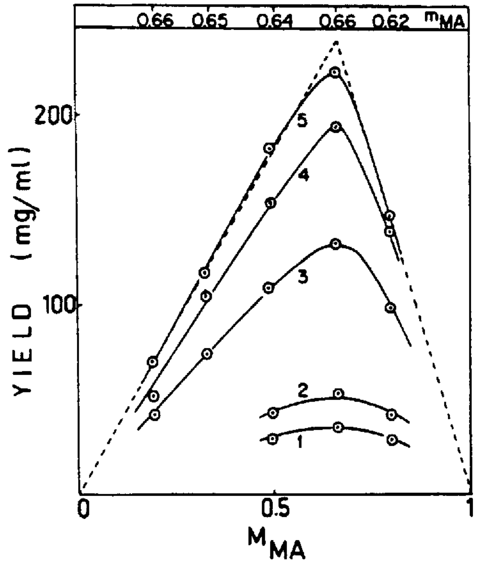


FIG. 14. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6×10^{-3} mole/liter. DVE-MA system in acetophenone. 1: 25 min; 2: 35 min; 3: 120 min; 4: 300 min; 5: 720 min.

$$\frac{d \text{ rate}}{da} = (m - a)^2 - a^2\left(\frac{k_1}{k_2} + \frac{k_1}{k_3}\right) \qquad (12)$$

and the maximum of the initial rate is observed when the derivative equals 0, i.e.

$$\left(\frac{1-M_a}{M_a}\right)^2 = \frac{k_1}{k_2} + \frac{k_1}{k_3} \qquad (13)$$

It is therefore not possible to determine both ratios k_1/k_2 and k_1/k_3

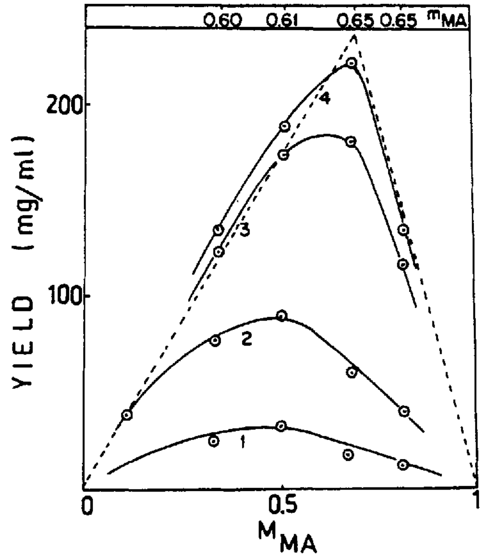


FIG. 15. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6×10^{-3} mole/liter. DVE-MA system in acetone. 1: 40 min; 2: 120 min; 3: 600 min; 4: 1200 min.

with only the experimental determination of M_a. However, if one assumes that the ratio k_1'/k_2' is comparable to the ratio k_1/k_2 (it does not mean that $k_1' = k_1$ and $k_2' = k_2$), it becomes possible to evaluate k_1/k_3. The results are presented in Table 1. Except in toluene, it was observed that $k_3 < k_2$; the addition of the first molecule of MA is faster than the second one; it can be concluded tentatively that the radical a· is more reactive than the radical a_c·. This conclusion, however, must be accepted only with caution because it was drawn after making several assumptions.

The Order of Polymerization

It has been observed that the equilibrium constant of the complex formation is generally very small; the concentration of complex is

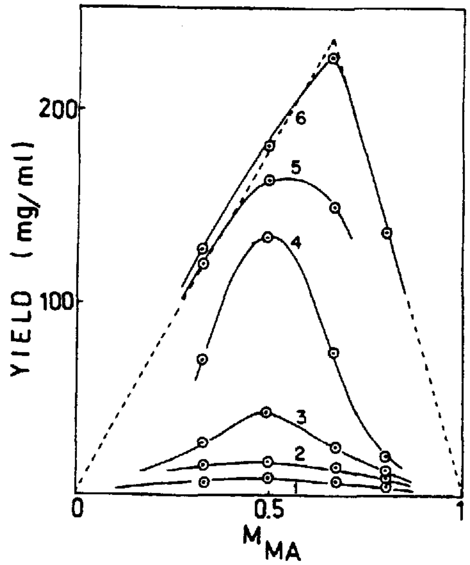


FIG. 16. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6×10^{-3} mole/liter. DVE-MA system in methylene chloride. 1: 10 min; 2: 12 min; 3: 15 min; 4: 20 min; 5: 40 min; 6: 120 min. Titration of these polymers was not possible due to their insolubility.

smaller than the concentration of the components. Therefore relation (2) becomes

$$Kab \simeq c \tag{14}$$

When the feed composition is kept constant (a/b = constant), the concentration of the complex is a function of the square of the total monomer concentration, a + b. If the complex is the reactive specie of the copolymerization, relation (1) shows that the rate depends also on the square of the total monomer concentration. An order of two is expected. On the other hand, if the polymerization occurs by successive additions of monomers, a first-order dependence is expected as shown in relations (5) and (11). Therefore, the study

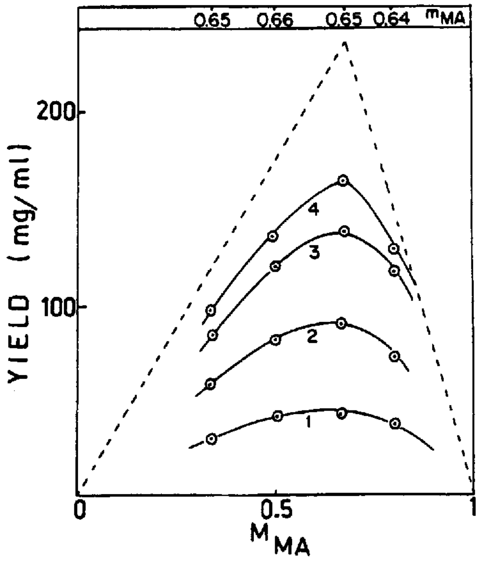


FIG. 17. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6×10^{-3} mole/liter. DVE-MA system in benzonitrile. 1: 60 min; 2: 120 min; 3: 210 min; 4: 300 min.

of the rate of polymerization as a function of the total monomer concentration when the feed composition is kept constant appears to be an interesting experimental approach for further examination of the concept of participation of the complex in the mechanism of copolymerization.

The rate can be expressed simply by

$$\text{rate} = \text{function of } (a + b)^n \qquad (15)$$

The order n was determined by high precision measurements. In each solvent and for each concentration condition the yield of polymer was measured after different times of polymerization; the slope of the plot of yield vs time gives the exact value of the initial rate

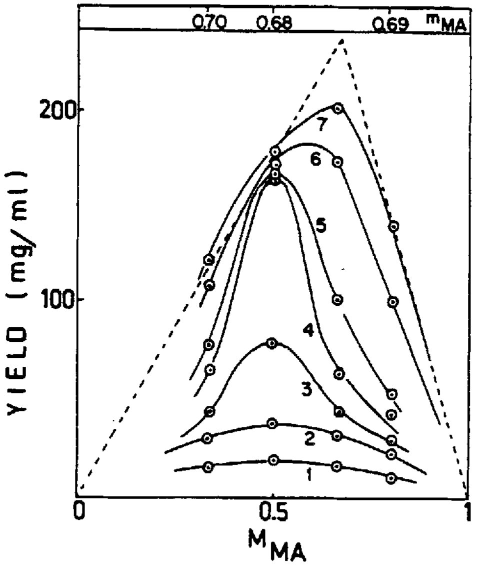


FIG. 18. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6×10^{-3} mole/liter. DVE-MA system in toluene. 1: 14 min; 2: 20 min; 3: 25 min; 4: 31 min; 5: 35 min; 6: 60 min; 7: 120 min.

expressed in terms of weight per volume and time. The log of the rate vs the log of the total monomer concentration permits the accurate determination of n. Examples of application of this method are given in Figs. 21 and 22. Note that the composition of the polymers is approximately constant so that an expression of the rate in terms of moles per volume and time instead of weight per volume and time will not affect the value of n. The details of the results of the rate study in each solvent and for each monomer concentration are tabulated in Tables 2a and 2b, while the orders n observed in each solvent are tabulated in Table 3.

In acetonitrile the experiments were carried out for two different feed compositions; n was found to be constant and is therefore not affected by the feed composition.

TABLE 2a. Summary of Results for the DVE-MA System[a]

Solvent	(DVE) + (MA) (moles/ liter)	M_{MA}	(AIBN) (moles/ liter × 10^3)	Initial rate (mg/ml-min)	m_{MA}	MW	N_{pm} (1/ml-min) (10^{-15})	$\%N_2$	N_R (2/ml-min) (10^{-15})	N_{pm}/N_R	$2N_{pm}/N_R$
Dimethyl formamide	4.5	0.20	6	0.30	0.63	1930	96.3	0.66	87.9	1.09	2.18
	2.7	0.20	6	0.126	0.63	-	-	0.23	12.4	-	-
	1.5	0.20	6	0.063	0.62	1420	28.6	0.62	17.0	1.56	3.12
	0.6	0.20	6	0.0168	-	-	-	1.56	6.46	-	-
	0.5	0.20	6	0.0096	0.65	-	-	-	-	-	-
	0.6	0.20	24	0.0491	-	-	-	-	-	-	-
	0.6	0.20	1.5	0.00616	-	-	-	-	-	-	-
Aceto-phenone	2.7	0.67	6	2.52	0.61	Ins	-	0.065	70.0	-	-
	0.9	0.67	6	0.26	0.53	Ins	-	0.135	15.0	-	-
	0.36	0.67	6	0.055	-	-	-	-	-	-	-
	0.3	0.67	6	0.037	0.55	1600	13.9	0.255	4.04	3.44	6.88
	0.36	0.67	24	0.171	-	-	-	-	-	-	-
	0.36	0.67	1.5	0.019	-	-	-	-	-	-	-

Acetone	2.7	0.33	6	0.77	0.58	Ins	-	0.095	31.4	-	-
	2.16	0.33	6	0.54	0.58	-	-	-	-	-	-
	1.62	0.33	6	0.46	0.56	Ins	-	0.085	16.7	-	-
	1.08	0.33	6	0.27	0.56	-	-	-	-	-	-
	0.54	0.33	6	0.15	0.57	Ins	-	0.16	11.1	-	-
	0.18	0.33	6	0.0611	-	-	-	0.205	5.97	-	-
	1.08	0.33	1.5	0.142	-	-	-	-	-	-	-
	1.08	0.33	0.375	0.08	-	-	-	-	-	-	-
Methylene chloride	2.7	0.50	6	3.84	0.68	Visc	-	0.05	82.5	-	-
	0.9	0.50	6	1.17	0.65	4840	141	0.085	42.7	3.4	6.8
	0.3	0.50	6	0.375	0.67	4250	53.1	0.180	29.0	1.80	3.6
	0.3	0.50	24	0.878	-	-	-	-	-	-	-
	0.3	0.50	1.5	0.216	-	-	-	-	-	-	-
	0.3	0.50	0.375	0.0985	-	-	-	-	-	-	-
Benzonitrile	2.7	0.67	6	1.11	0.68	7600	87.9	0.125	59.3	1.48	2.96
	0.9	0.67	6	0.176	0.66	5870	18.1	0.215	16.2	1.11	2.22
	0.3	0.67	6	0.036	0.61	1290	16.7	1.06	16.4	1.02	2.04
	0.12	0.67	6	0.0126	-	-	-	2.615	14.1	-	-

(continued)

TABLE 2a. Summary of Results for the DVE-MA System (Continued)

Solvent	(DVE) + (MA) (moles/ liter)	M_{MA}	(AIBN) (moles/ liter × 10^3)	Initial rate (mg/ml-min)	m_{MA}	MW	N_{pm} (1/ml-min) (10^{-15})	%N_2	N_R (2/ml-min) (10^{-15})	N_{pm}/N_R	$2N_{pm}/N_R$
Benzonitrile (cont)	0.9	0.67	1.5	0.431	-	-	-	-	-	-	-
	0.9	0.67	0.375	0.175	-	-	-	-	-	-	-
Toluene	2.7	0.50	6	3.72	0.65	Visc	-	0.085	135	-	-
	0.9	0.50	6	1.22	0.65	5000	132	0.055	28.8	5.09	10.18
	0.3	0.50	6	0.32	0.62	4350	44.2	0.160	22.0	2.00	4.00
	0.1	0.50	6	0.0655	-	-	-	0.165	4.64	-	-
	0.9	0.50	1.5	0.431	-	-	-	-	-	-	-
	0.9	0.50	0.375	0.175	-	-	-	-	-	-	-
Acetonitrile	2.7	0.67	6	2.9	0.67	-	-	-	-	-	-
	1.08	0.67	6	0.615	0.64	-	-	-	-	-	-
	0.45	0.67	6	0.102	0.63	-	-	-	-	-	-
	0.225	0.67	6	0.030	0.64	-	-	-	-	-	-
	1.08	0.67	1.5	0.198	-	-	-	-	-	-	-

1.08	0.67	0.375	0.065	-	-	-	-	-	-	-
2.7	0.33	6	2.65	0.67	Ins	-	0.09	102	-	-
1.08	0.33	6	0.68	0.64	11000	37.2	0.125	36.5	1.02	2.04
0.45	0.33	6	0.102	0.64	6900	8.9	0.32	14.0	0.63	1.26
0.225	0.33	6	0.025	0.63	4300	3.5	0.57	6.12	0.57	1.14

---

[a] M_{MA} molar fraction of MA in the feed; m_{MA} = molar fraction of MA in the copolymer; MW = molecular weight; N_{pm} = number of polymeric molecules; N_R = number of butyronitrile radicals intiating the polymerization.

TABLE 2b. Summary of the Results for the EVE-MA System[a]

Solvent	(EVE) + (MA)	M_{MA}	(AIBN) (moles/liter × 10^3)	Initial rate (mg/ml-min)	m_{MA}	MW
Acetophenone	2.7	0.20	6	2.78	0.51	16700
	0.9	0.20	6	0.368	0.52	7500
	0.3	0.20	6	0.0438	0.50	4520
	0.9	0.20	24	0.96	-	-
	0.9	0.20	1.5	0.108	-	-
Methylene chloride	2.7	0.67	6	3.28	0.51	-
	0.9	0.67	6	1.52	0.57	-
	0.3	0.67	6	0.465	0.57	15000
	0.3	0.67	24	0.98	-	-
	0.3	0.67	1.5	0.18	-	-

[a] M_{MA} = molar fraction of MA in the feed; m_{MA} = molar fraction of MA in the copolymer; MW = molecular weight; N_{pm} = number of polymeric molecules; N_R = number of butyronitrile radicals initiating the polymerization.

TABLE 3. Dielectric Constant of the Solvent and Value of the Different Orders of the Polymerization

Solvent	Dielectric constant	DVE-MA				EVE-MA	
		n	m	p	q	n	m
Dimethyl formamide	37	1.59	0.75	0.95	0.88	-	-
Acetophenone	17.4	1.91	0.79	1.25	0.93	1.90	0.77
Acetone	20.7	1.00	0.46	0.45	0.80	-	-
Methylene chloride	9.08	1.06	0.52	0.47	0.82	0.92	0.59
Benzonitrile	25.2	1.50	1.00	0.41	1.09	-	-
Toluene	2.43	1.15	0.65	0.81	0.63	-	-
Acetonitrile[a]	37.5	1.93	0.83	1.13	1.00	-	-

[a] For $M_{MA} = 0.33$ or 0.67.

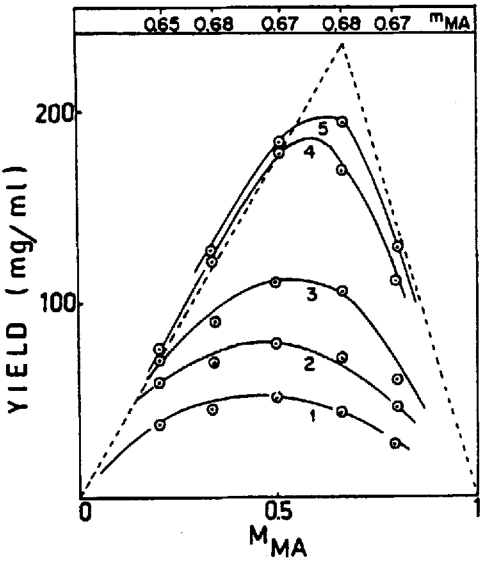


FIG. 19. Yield and molar fraction of MA in the copolymer (m_{MA}) vs the molar fraction of MA in the feed (M_{MA}). Total monomer concentration = 2.7 moles/liter. (AIBN) = 6×10^{-3} mole/liter. DVE-MA system in acetonitrile. 1: 30 min; 2: 45 min; 3: 60 min; 4: 120 min; 5: 240 min.

The order n of the total monomer concentration takes different values from 1 to 2, and seems to increase with an increase of the dielectric constant of the solvent (Fig. 23). Even if it is assumed that the mechanism of polymerization is by successive addition of monomers (Order 1) in some solvents while in others the charge-transfer complex is involved (Order 2), the results are not consistent with this viewpoint. Indeed, it is generally found that the equilibrium constant for complexation decreases with an increase of dielectric constant of the solvent. Therefore, a decrease of the participation of the charge-transfer complex and a decrease of the order would be expected for an increase of the dielectric constant of the solvent. However, the reverse was observed: in acetonitrile (dielectric constant = 37), n = 1.93; in methylene chloride (dielectric constant = 9.08), n = 1.06; in toluene (dielectric constant = 2.43),

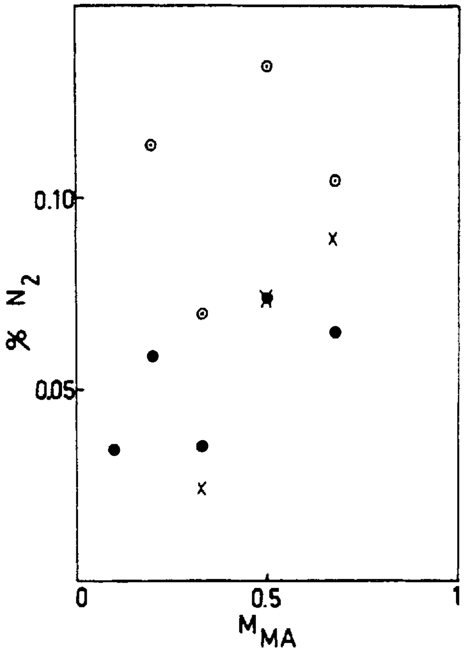


FIG. 20. Nitrogen percentage of the polymers vs the feed composition. Total monomer concentration = 2.7 moles/liter. EVE-MA system in acetophenone (solid circles), in methylene chloride (cross points), and in acetonitrile (open circles).

n = 1.15. It appears therefore that the order n is probably an apparent order and that other factors are involved. For this reason the dependence of the AIBN concentration on the rate of polymerization was determined. Similar methods were used for the accurate determination of the order m of the AIBN concentration. Examples are given in Figs. 24 and 25, while the results are presented in Tables 2 and 3.

The order m in different solvents varies from 0.5 to 1 and seems also to increase with an increase of the dielectric constant of the solvent. But the most significant observation lies in the fact that the orders n and m follow exactly the same trend of variations in the different solvents (except for one point). Seven solvents were

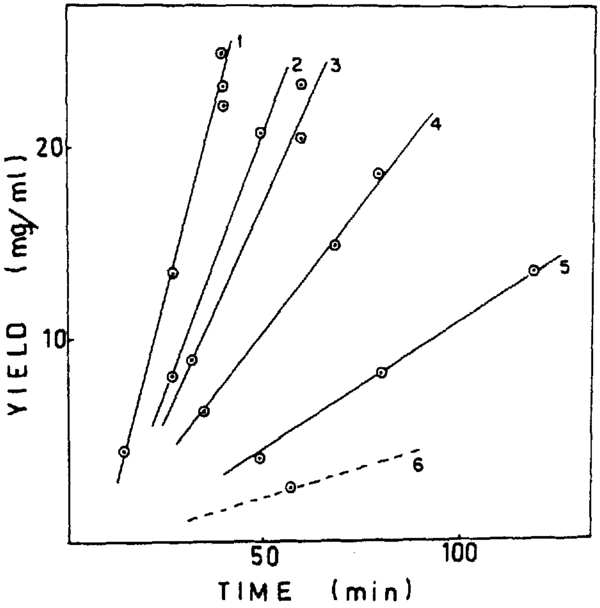


FIG. 21. Yield vs time, DVE-MA system in acetone. (AIBN) = 6×10^{-3} mole/liter. $M_{MA} = 0.33$. Total monomer concentration = 2.7 (1), 2.16 (2), 1.62 (3), 1.08 (4), 0.54 (5), and 0.18 mole/liter (6).

used; the probability that two groups of seven numbers are in the same order is 1/7! = 1/5040. Therefore, it is practically certain that n and m are correlated.

The efficiency of the initiator as a function of the monomer concentration was determined. From the nitrogen analysis of the polymers (the presence of nitrogen is evidently due to the initiation by the butyronitrile radicals; but in the case of solvents containing nitrogen, the presence of nitrogen can also be due to transfer reactions on the solvent or to occlusion of solvent molecules by the polymer), and from the rate of polymerization, it is possible to determine the rate of incorporation of nitrogen into the polymer; from this rate, and the atomic weight of nitrogen and Avogadro's number, it is therefore possible to determine the number, N_R, of nitrogen atoms bound to the polymer per volume

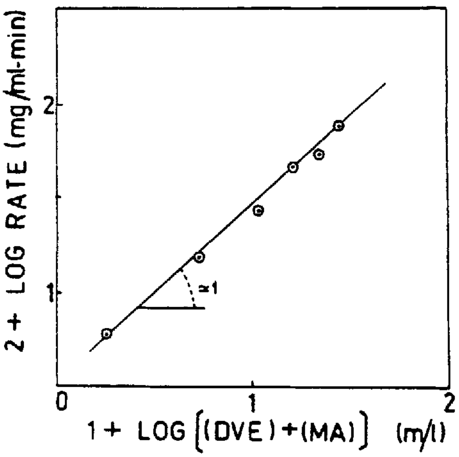


FIG. 22. Log of initial rate vs log of the total monomer concentration. Initial rate from Fig. 21.

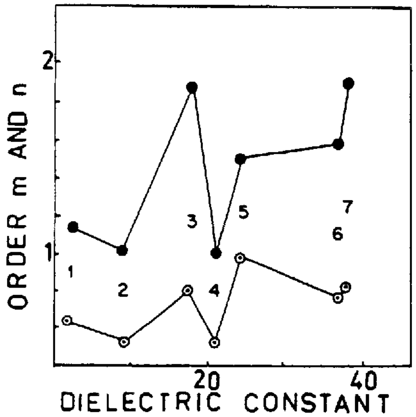


FIG. 23. Order n of the monomer concentration (solid circles) and order m of the AIBN concentration (open circles) vs the dielectric constant of the solvent. 1: Toluene; 2: methylene chloride; 3: acetophenone; 4: acetone; 5: benzonitrile; 6: dimethyl formamide; 7: acetonitrile.

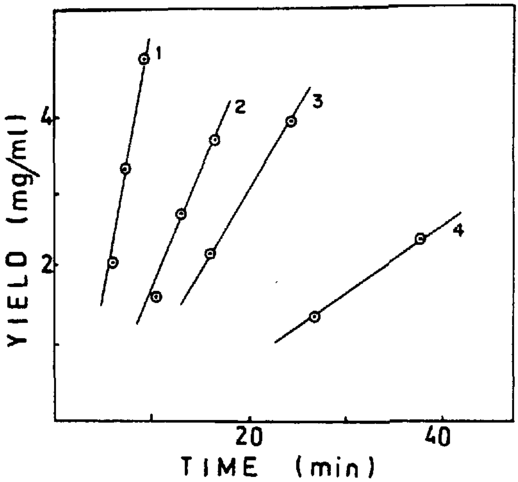


FIG. 24. Yield vs time, DVE-MA system in methylene chloride. Total monomer concentration = 0.3 mole/liter. M_{MA} = 0.5. (AIBN) = 2.4×10^{-3} (1), 6×10^{-3} (2), 1.5×10^{-3} (3) and 0.375×10^{-3} mole/liter (4).

and time unit. Neglecting the above restrictions in the case of nitrogen-containing solvents, the number N_R is evidently equal to the number of butyronitrile radicals effectively initiating the polymerization. The values of N_R are given in Table 2. It is observed that N_R increases with an increase of the total monomer concentration; the higher the monomer concentration, the higher is the concentration of growing radicals. The number N_R can be expressed by

$$N_R = \text{function of } (M)^p \qquad (16)$$

M represents the total monomer concentration.

Since the efficiency of the initiator is equal to the number N_R divided by the total number of radicals produced by the decomposition of the initiator, the efficiency is also a function of $(M)^p$. The order p

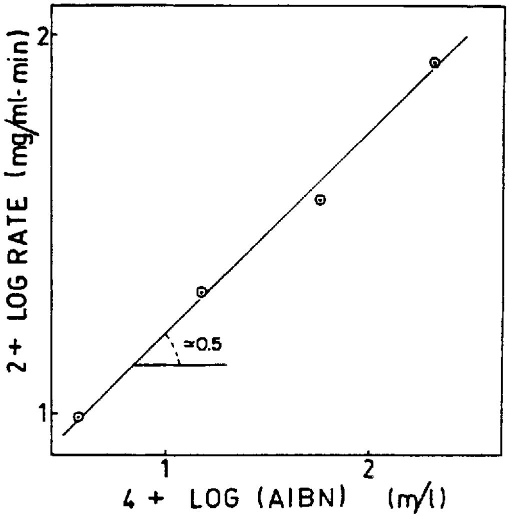


FIG. 25. Log of the initial rate vs log of the AIBN concentration. Initial rate from Fig. 24.

is found by plotting the log of N_R vs the log of the total monomer concentration. An example is given in Fig. 26. The values of p are given in Table 3. It should be pointed out that the values of p are susceptible to relatively large errors since the nitrogen percentages of the polymers are generally very low.

The classical expression of the rate of polymerization initiated by a radical initiator (AIBN) is generally given by

$$\text{rate} = \text{function of } (M)^q\,[f(\text{AIBN})]^m$$

or

$$= \text{function of } (M)^q\,[(M)^p(\text{AIBN})]^m$$

or

$$= \text{function of } (M)^{q+pm}(\text{AIBN})^m \qquad (17)$$

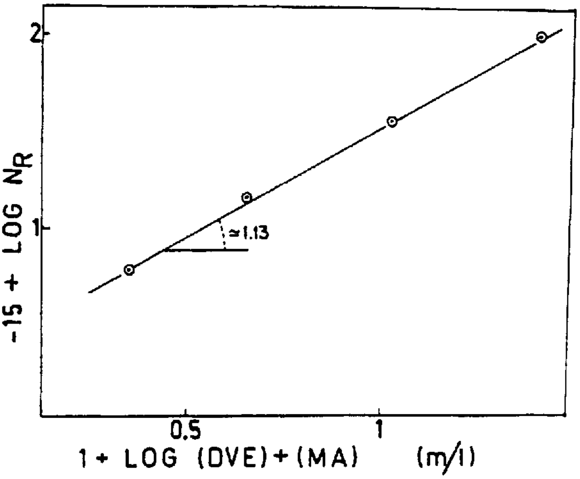


FIG. 26. Log of the number of butyronitrile radicals initiating the polymerization (per ml/min) vs the total monomer concentration. DVE-MA system in acetonitrile. (AIBN) = 6×10^{-3} mole/liter. $M_{MA} = 0.33$.

While n represented the apparent order of monomer concentration, q represents here the true order, and one has

$$n = q + pm \tag{18}$$

From the experimental determinations of n, p, and m, q is easily determined. Values of q are recorded in Table 3.

As observed, the values of q are generally close to 1 except in toluene where q is lower. This result is very interesting because an order of 1 is generally expected for radical-initiated polymerization when initiator efficiency and other factors can be neglected. Therefore, it is shown that the kinetic data can be explained without the necessary participation of a charge-transfer complex. The DVE-MA copolymerization seems to follow an usual mechanism of polymerization with specific interaction between the monomers and the radicals of different polarity leading to alternating copolymers. The deviations of q from unity can be explained by considering the fact that errors of 5% on n, p, and m can lead easily to errors of 20% on q.

Additional experiments were carried out for the EVE-MA copolymerization in acetophenone and methylene chloride. In both of these solvents the orders n and m are similar to those obtained in the DVE-MA copolymerization. One concludes that the mechanism of the EVE-MA system is similar, and the same conclusions can be drawn.

The influence of the solvent on the mechanism of termination and in the transfer reaction was also considered. It has been pointed out that m varies from 0.5 to 1 and increases with the dielectric constant of the solvent. In acetophenone and benzonitrile, m is higher than expected. An order of 0.5 indicates a termination by a coupling reaction between growing radicals, while an order of 1.0 indicates a noncoupling termination (reaction between a radical and another specie, or no termination at all). It appears therefore that there is a change in the termination mechanism with the dielectric constant of the solvent; in high dielectric constant solvents, noncoupling termination is more probable, while in low dielectric constant solvents, termination by coupling appears to predominate. In the absence of chain transfer the number of polymeric chains formed per unit time, N_{pm}, is equal to the number of initiating radicals formed per unit time, N_R, for termination by a noncoupling mechanism or to one half of this number for termination by a coupling mechanism:

$$\text{For noncoupling termination,} \quad N_{pm} = N_R \text{ or } N_{pm}/N_R = 1 \qquad (19)$$

$$\text{For coupling termination,} \quad N_{pm} = 1/2\, N_R \text{ or } 2N_{pm}/N_R = 1 \qquad (20)$$

The number N_{pm} is determined from the rate of polymerization, the molecular weight measurements, and Avogadro's number. The results are recorded in Table 2. It was observed that $N_{pm} > N_R$ (it follows that $2N_{pm} \gg N_R$) (an exception was observed in acetonitrile). Therefore, it seems that transfer reactions occur by an increase in the number of polymeric molecules relative to the number of radicals initiating the polymerization.

The extent of the transfer can be evaluated by considering the ratio to be N_{pm}/N_R when the order is $m = 1$ as in benzonitrile, and the ratio to be $2N_{pm}/N_R$ when the order is $m = 0.5$ as in methylene chloride. It was observed that the transfers occurred more often in solvents of low dielectric constant than in solvents of high dielectric constant. Moreover, it was observed that the transfers increased with an increase of the total monomer concentration (except in dimethyl formamide).

All of these observations suggest the following picture for the transfer and termination processes. A growing radical is solvated by monomer or solvent molecules, but solvation by monomer molecules is relatively favored in solvents of low dielectric constant. Transfer to monomer occurs easier and termination by coupling predominates. In solvents of high dielectric constant, less transfer to monomer occurs and noncoupling termination predominates due to the high solvation of the radicals by the solvent molecules. It is quite evident that this picture represents only a general trend. Finally, the fact that the order m is greater than expected in acetophenone and benzonitrile can be explained by considering that these solvents possess some electron-acceptor character and are capable of a high degree of solvation; noncoupling termination now becomes predominant.

TABLE 4. Phase of the Polymerization in Different Solvents (see the respective concentrations in Table 2)

	Phase	
Solvent	DVE-MA	EVE-MA
Dimethyl formamide	Hom	Hom
Acetophenone	Hom Het	Hom
Acetone	Hom Het	Hom
Methylene chloride	Het	Het
Benzonitrile	Hom Het	Hom
Toluene	Het	Het
Acetonitrile	Het	Hom

The Phase of Polymerization

With respect to the phase of polymerization, it has been observed that the rate of polymerization with precipitation of the polymer during polymerization (heterogeneous phase) is generally faster than the rate of polymerization without precipitation (homogeneous phase). However, in some solvents the phase depends on the total monomer concentration; however, no specific change of the rate was observed when the polymerization became heterogeneous. The plot of log of rate vs log of monomer concentration remained linear regardless of the phase. An example is given in Fig. 22. At the higher concentration, the polymerization is heterogeneous, and at the lower, homogeneous. The details on the phase study are summarized in Table 4.

ACKNOWLEDGMENTS

We wish to acknowledge financial support of this work by the National Institutes of Health under Grant No. CA06838 and by the National Science Foundation in the form of a fellowship to one of us (BZ) made available through a Center of Excellence Grant to the University of Florida.

REFERENCES

[1] J. M. Barton, G. B. Butler, and E. C. Chapin, J. Polym. Sci., Part A, 3, 501 (1965).
[2] G. B. Butler, G. Vanhaeren, and M. F. Ramadier, J. Polym. Sci., Part A-1, 5, 1265 (1967).
[3] G. B. Butler and K. C. Joyce, J. Polym. Sci., Part C, 22, 45 (1969).
[4] G. B. Butler and A. F. Campus, J. Polym. Sci., Part A-1, 8, 545 (1970).
[5] K. Fujimori, Ph.D. Thesis, University of Florida, Gainesville, Florida, 1971.
[6] P. Job, C. R. Acad. Sci., Paris, 190, 928 (1925).
[7] H. A. Benesi and J. H. Hildebrand, J. Amer. Chem. Soc., 71, 2703 (1949).

[8] W. G. Barb, Trans. Faraday Soc., 49, 143 (1953).
[9] C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, J. Amer. Chem. Soc., 70, 1537 (1948).

Accepted by editor March 3, 1972
Received for publication June 22, 1972