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Studies in Cyclocopolymerization. VIII. Solvent Effects in Cyclocopolymerization of Maleic Anhydride with Divinyl Ether

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Studies in Cyclocopolymerization. VIII. Solvent Effects in Cyclocopolymerization of Maleic Anhydride with Divinyl Ether*

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ABSTRACT

Solvent effects in the cyclopolymerization of maleic anhydride (MA) with divinyl ether (DVE) were systematically studied. Evidence is presented which supports a charge-transfer (CT) complex formed between the comonomers as the active species in the cyclocopolymerization. The equilibrium constants (K) of CT complexation with MA was measured in n-heptane by UV spectrophotometry for tetrahydrofuran, ethyl vinyl ether, DVE, furan, and dihydropyran. K-values increased in the above order. K of the MA-DVE pair was measured by UV and NMR in polyhaloalkanes as solvents. K-values decreased with increase of the dielectric constant of the solvent. The rate of copolymerization and number-average molecular weights decreased in more polar solvents. The initial rate was about 100 times faster

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in $CHCl_3$ than in DMF. In dilute solution, $[M_1 + M_2] = 0.57$ mole/liter, the initial overall rate of copolymerization was maximum in DVE-rich feed in $CHCl_3$, CH_2Cl_2, and DMF. Kinetical derivation failed to explain the rate profile. Though still open to question, strong solvation of MA by the solvent has been proposed as an explanation. The overall rate of copolymerization was proportional to one-half order of AIBN concentration in DMF. The overall energy of activation was 27 kcal/mole in $CHCl_3$ and in DMF. Thermal autopolymerization, photopolymerization, and γ-ray polymerization of the MA-DVE pair in bulk gave the same 2:1 (= [MA]:[DVE]) copolymer. Retardation of rate by hydroquinone was observed in thermal autopolymerization. The dative state of the CT complex was considered to be the initiating species.

INTRODUCTION

The course of cyclocopolymerization of 1,4-dienes such as divinyl ether (DVE) and certain monoolefins such as maleic anhydride (MA) has now been well established [1, 2]. During the course of an investigation of this type of cyclocopolymerization, Butler and Joyce [3] proposed participation of a charge-transfer (CT) complex in the cyclocopolymerization mechanism on the basis that MA-DVE and fumaronitrile (FN)-DVE pairs were found to form CT complexes which were detected in their UV spectra, the monoolefins being the acceptors for DVE. Butler and Campus [4] investigated CT-complex formation of a number of monoolefin-1,4-diene acceptor-donor pairs which undergo cyclocopolymerization, such as MA-DVE, FN-DVE, and MA-dimethyldivinylsilane, using UV and NMR. They found that the stoichiometry of complexation was always 1:1, while these three pairs formed 2:1 alternating cyclocopolymers. They found dilution effects on the copolymer composition of FN-DVE pair in support of the participation of the CT complex in the cyclocopolymerization.

Solvent effects on CT complexation and cyclocopolymerization were studied systematically in the present paper using the MA-DVE pair as the model system, since this pair has been studied most extensively. The purpose was to determine whether such studies would provide further evidence in support of the participation of the CT complex in the cyclocopolymerization mechanism.

RESULTS AND DISCUSSION

Charge-Transfer Complex

The CT complex of an acceptor-donor pair is in equilibrium with the free components. The CT complex exists in resonance between the no-bond state and the dative state; thus the wave functions of the CT-complex [ψ_{CT}] can be expressed as a linear combination of wave functions of the no-bond state [ψ(A, D)] and the dative state [$\psi(\cdot A^{\cdot -}_{,} D^{\cdot +})$] [5] (Eqs. (1) and (2).

$$A + D \underset{}{\overset{K}{\rightleftharpoons}} \overset{\text{charge-transfer complex}}{[\underset{\text{no-bond}}{(A, D)} + \underset{\text{dative}}{(\cdot A^{\cdot -}_{,} D^{\cdot +})}]} \tag{1}$$

$$\psi_{CT} = a\psi(A, D) + b\psi(\cdot A^{\cdot -}_{,} D^{\cdot +}) \tag{2}$$

$a \gg b$ in the ground state of the complex, and $b \gg a$ in the excited state of the complex.

In the UV the CT complex shows its own characteristic absorption near the absorption of one of the components. The equilibrium constant (K) of complexation and the molar extinction coefficient (ϵ) of a CT complex can be measured by using the Scott equation (Eq. 3) [6], which is

$$\frac{[A][D]l}{d} = \frac{1}{\epsilon K} + \frac{1}{\epsilon}[D] \tag{3}$$

where [A] = acceptor concentration (mole/liter), [D] = donor concentration (mole/liter), d = absorbancy, and l = path length (cm), a rearranged equation of Benesi and Hildebrand [7].

The equilibrium constant and extinction coefficients were measured in n-heptane for a number of donor compounds structurally related to DVE, using MA as the acceptor (Table 1). The absorption of the MA-DVE complex and the Scott plot of MA-DVE in n-heptane are shown in Figs. 1 and 2, respectively.

TABLE 1. UV Study of Charge-Transfer Complex of Some Ethers with Maleic Anhydride in n-Heptane at 24°C

Donor	$[A] \times 10^3$ (mole/liter)	[D] range (mole/liter)	λ_{max} (mμ)	ε (liter/mole cm)	K (liter/mole)
Tetrahydrofuran	1.003	0.488-4.88	241	1.3×10^3	8.6×10^{-2}
Ethyl vinyl ether	2.507	2.631-9.21	270	8.1×10^2	1.5×10^{-1}
Divinyl ether	1.003	0.828-3.04	270	5.6×10^2	1.8×10^{-1}
Furan	1.003	0.688-3.44	287	3.3×10^2	4.7×10^{-1}
Dihydropyran	1.003	0.572-3.14	295	5.9×10^2	1.1×10^{-1}

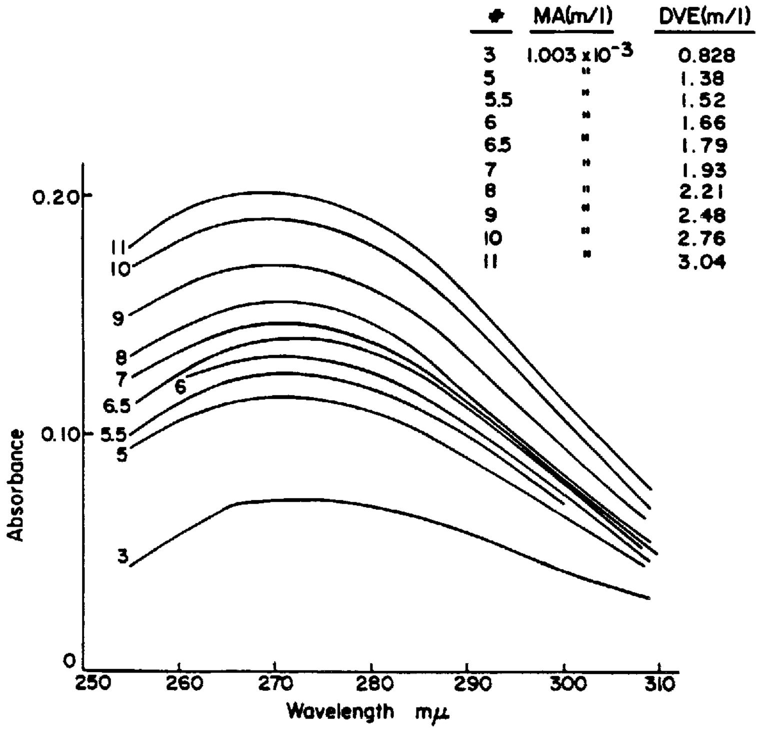


FIG. 1. Charge-transfer absorption of MA-DVE in n-heptane at 24°C.

The energy of the CT transition, which can be calculated from λ_{max}, is a function of, among other minor variables, the electron affinity of the acceptor (E_A) and the ionization potential (I_D) of the donor [8]. Empirically, the CT transition energy is proportional to the ionization potentials of the donors when complexing with the same acceptor:

$$h\nu_{CT} = mI_D + n \tag{4}$$

where m and n are constants.

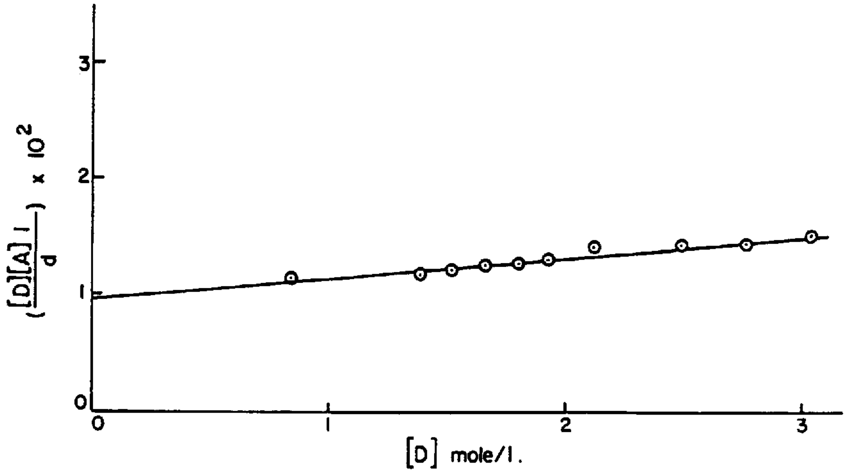


FIG. 2. Scott plot of MA-DVE complex in n-heptane at 270 mμ, at 24°C.

Table 1 shows that I_D is smaller when there is more orbital overlap between the orbitals of nonbonding electrons of the oxygen and π-electrons of the vinyl group of an ether. The reversed order of furan and dihydropyran may be due to the aromaticity of furan, which lowers the energy level of the highest occupied molecular orbital of furan. It is interesting to note that there is a somewhat parallel relation between λ_{max}, hence CT transition energy, and the equilibrium constant of complexation.

Since CT complexation follows polar association of the components, the more polar solvent would reduce the magnitude of K. The K-values of MA-DVE were measured by UV and by NMR using the Hanna-Ashbaugh equation [9] (Eq. 5), in the latter, to determine the change of the K-values by the solvent polarities. Structurally related solvents were used with the exception of n-heptane to avoid discontinuous changes in solvating ability.

When the concentration of MA is very small, the chemical shift of the hydrogens of MA is shifted by varying the concentration of DVE and appears at an intermediate position between free MA and completely complexed MA; MA being in dynamic equilibrium between these states.

$$\frac{1}{\Delta_{obsd}^{A}} = \frac{1}{Q\Delta_{CT}^{A}}\frac{1}{[D]} + \frac{1}{\Delta_{CT}^{A}} \tag{5}$$

Where $\Delta_{obsd}^{A} = \delta_{obsd}^{A} - \delta_{o}^{A}$ is the difference between the chemical shift of the acceptor protons in complexing media (δ_{obsd}^{A}) and the shift of the acceptor in uncomplexed form (δ_{o}^{A}), $\Delta_{CT}^{A} = \delta_{CT}^{A} - \delta_{o}^{A}$, is the difference in the shift of the acceptor protons in pure complex (δ_{CT}^{A}) and free acceptor, and [D] is the concentration of the donor which has to be always much greater than the acceptor concentration in order that Q = K, the equilibrium constant of complexation. The Hanna-Ashbaugh plots and the Scott plot are shown in Figs. 3, 4, and 5, respectively. The results are shown in Table 2. The equilibrium

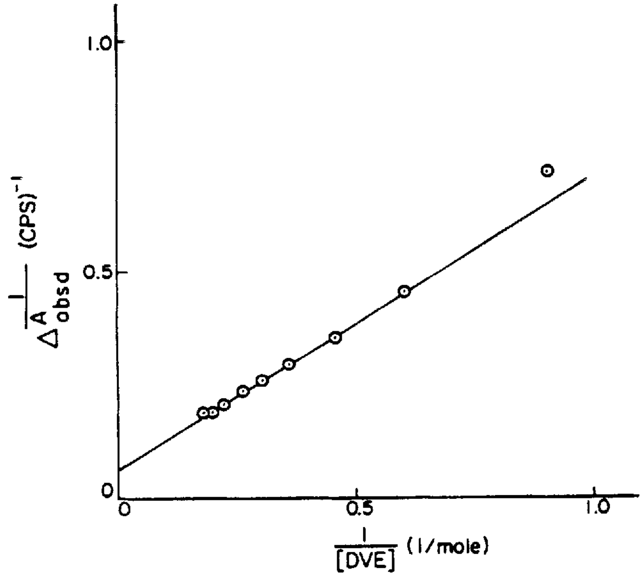


FIG. 3. Hanna-Ashbaugh plot of MA-DVE complex in CCl$_4$ at 38°C.

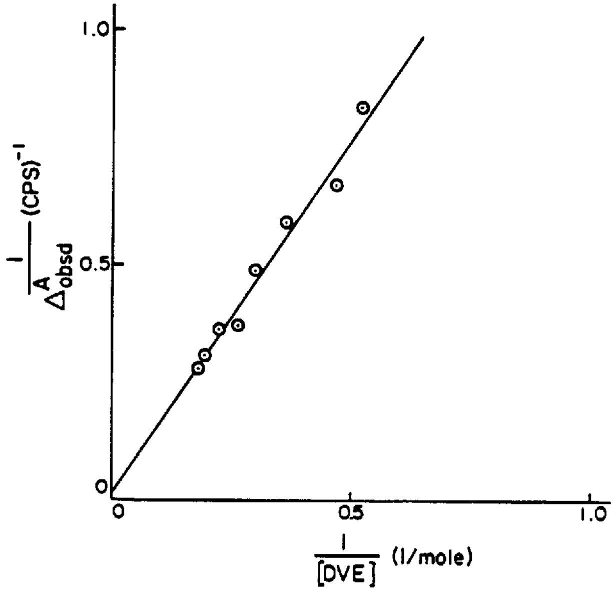


FIG. 4. Hanna-Ashbaugh plot of MA-DVE complex in CH_2Cl_2 at 38°C.

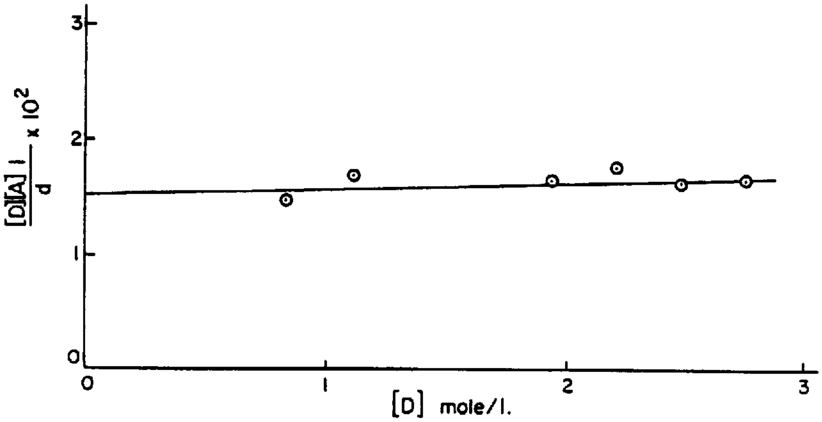


FIG 5. Scott plot of MA-DVE complex in CH_2ClCH_2Cl at 272 mμ, at 24°C.

TABLE 2. Equilibrium Constant of Complexation of the MA-DVE Pair in Various Solvents

Solvent	Dielectric constant [10]	K	Temp (°C)	ϵ	Method/λ_{max} (mμ)	Refs.
n-Heptane	1.924	1.08×10^{-1}	24	5.55×10^2	UV/270	
CCl_4	2.238	9.8×10^{-2}	38		NMR[a]	
$CHCl_3$	4.806	3.6×10^{-2}	24		NMR	4
CH_2Cl_2	9.08	1.4×10^{-2}	38		NMR[a]	
CH_2Cl_2	9.08	1.4×10^{-2}	24	2.75×10^3	UV/275	3
CH_2ClCH_2Cl	10.36	1.3×10^{-2}	24	5.0×10^3	UV/272	

[a] The range of concentrations of MA and DVE used for the measurement was: in CCl_4, $[MA] < 9.03 \times 10^{-4}$ mole/liter, $[DVE] = 1.104$-5.52 mole/liter; in CH_2Cl_2, $[MA] < 1.18 \times 10^{-3}$ mole/liter, $[DVE] = 1.38$-5.52 mole/liter.

constant decreased with increase of polarity of solvents. The same effect has been observed by other authors for various CT complexes [11, 12].

Rate of Copolymerization and Polarity of Solvent

If the CT complex is the polymerizing species in the cyclocopolymerization of the MA-DVE pair, the rate of polymerization should be greater with higher K-values; that is, with the same concentrations of comonomers and initiator, and the same reaction conditions are chosen in each polymerization, the rate should be greater the higher the concentration of polymerizing species in the system, thus producing higher molecular weight polymer. This point was tested by carrying out the copolymerization using solvents of widely different dielectric constants. The results are shown in Figs. 6 and 7 and Table 3.

One sealed polymerization tube was used for each solvent, and the polymerization was carried out in a thermostatted oil bath for a measured period of time. The yield was obtained by weighing the purified copolymer.

The effect of the polarity of the polymerization medium is evident, suggesting the importance of the CT complex in this copolymerization. As shown in Table 2, the more polar solvent results in a lower K-value, and also a lower rate of polymerization.

Initial Rate of Copolymerization at [MA]/[DVE] = 1

The initial rate of copolymerization was determined in $CHCl_3$ (dielectric constant = 4.806) and in DMF (dielectric constant = 37) at 50, 60, and 70°C. Figures 8 and 9, respectively, show time-conversion curves at the three temperatures for these solvents. The same reaction conditions were used: viz., $[M_1 + M_2] = 1$, and $[\text{AIBN}] = 2.38 \times 10^{-3}$ mole/liter. The polymerization reaction was carried out in a sealed tube and was stopped after a period of time by opening the tube and pouring the contents into a large amount of nonsolvent. The slope of the tangent line as calculated from the graph was taken as the initial rate of polymerization. The results are summarized in Table 4. The difference in the initial rate is

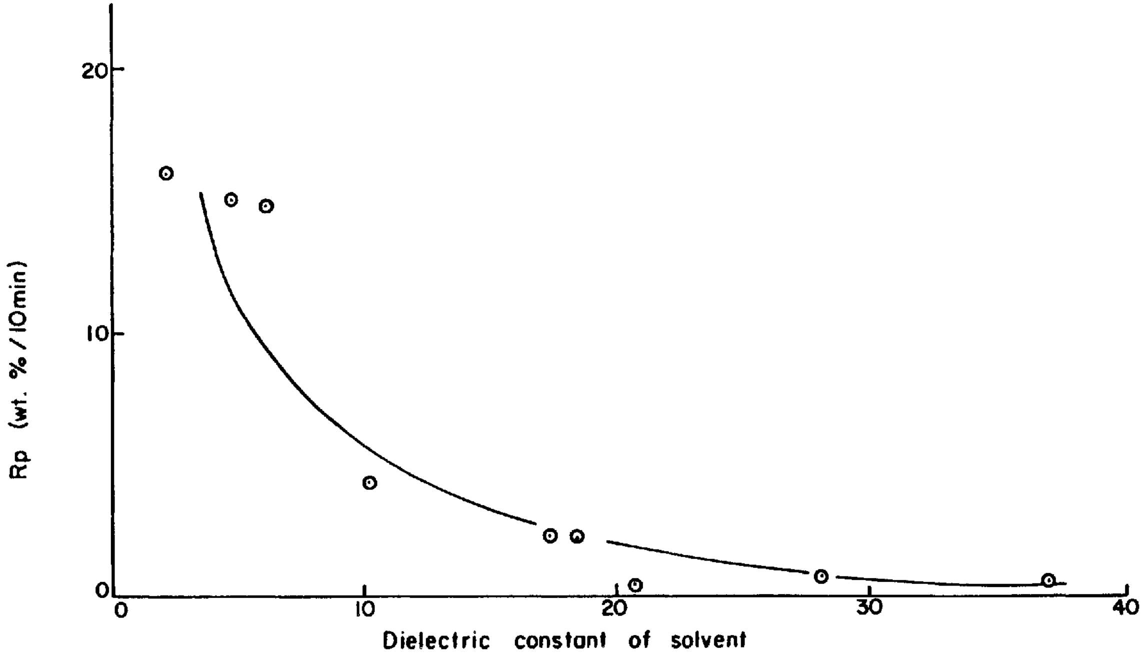


FIG. 6. Rate of copolymerization of MA-DVE in various solvents. $[M_1]/[M_2] = 1$, $[M_1 + M_2] = 1.28$ mole/liter, $[\mathrm{AIBN}] = 1.07 \times 10^{-2}$ mole/liter at 60°C.

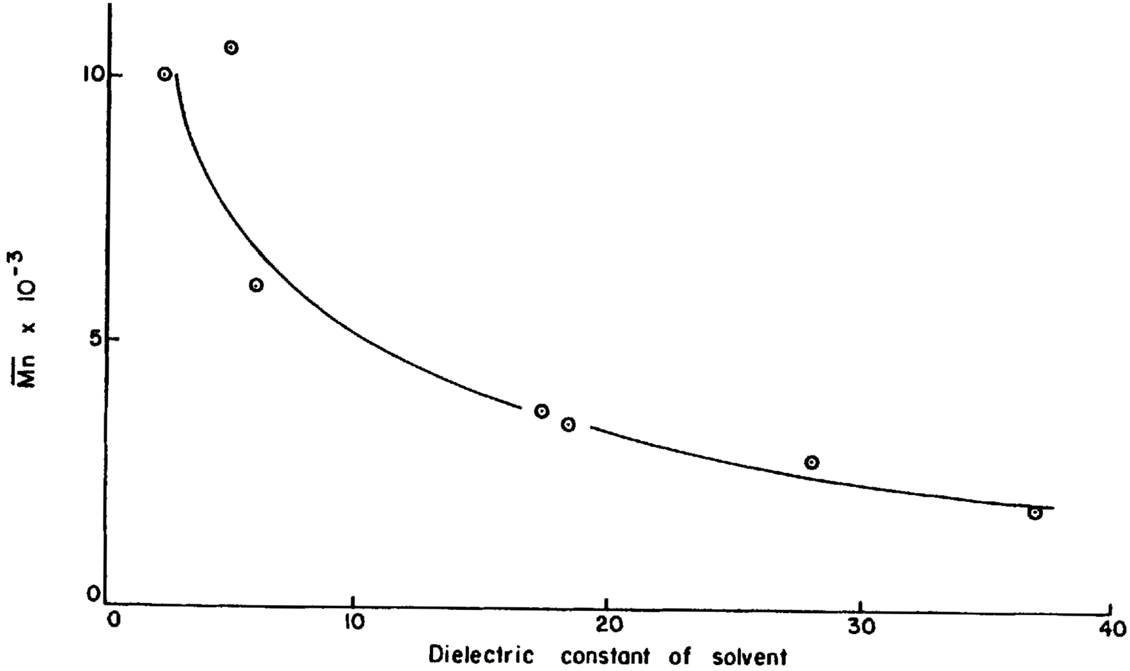


FIG. 7. Number-average molecular weight of copolymer of MA-DVE prepared in various solvents. $[M_1]/[M_2] = 1$, $[AIBN] = 1.07 \times 10^{-2}$ mole/liter, $[M_1 + M_2] = 1.28$ mole/liter at 60°C.

TABLE 3. Rate of Copolymerization of MA-DVE in Various Solvents[a]

Run	Solvent	Dielectric constant [10]	Yield (wt%/10 min)	$\overline{M}_n \times 10^{-3}$
M-D-52	Dioxane	2.209	16.0	10.0
M-D-52	Chloroform	4.806	14.9	10.5
M-D-52	Ethyl acetate	6.02	14.8	6.0
M-D-52	Ethylene chloride	10.36	4.20	
M-D-51	Acetophenone	17.4	2.24	3.7
M-D-51	Methyl ethyl ketone	18.51	2.20	5.3
M-D-51	Acetone	20.7	0.42	
M-D-51	Nitromethane	28.06	0.74	2.8
M-D-51	Dimethyl formamide	37	0.44	1.9

[a] $[M_1 + M_2] = 1.28$ mole/liter. $[M_1]/[M_2] = 1$, at 60°C. $[\mathrm{AIBN}] = 1.07 \times 10^{-2}$ mole/liter.

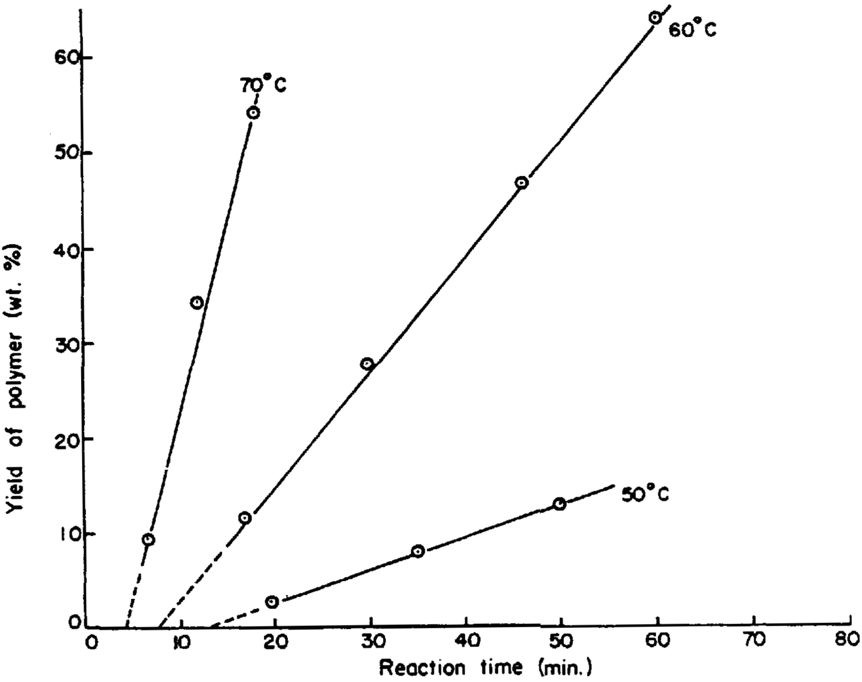


FIG. 8. Initial rate of copolymerization of MA-DVE in $CHCl_3$. $[M_1 + M_2] = 5.68 \times 10^{-1}$ mole/liter, $[M_1]/[M_2] = 1$, [AIBN] = 2.38×10^{-3} mole/liter.

TABLE 4. Initial Rate of Copolymerization of MA-DVE[a]

In $CHCl_3$		In DMF	
Temp. (°C)	R_p (mole/liter sec)	Temp. (°C)	R_p (mole/liter sec)
50	3.13×10^{-5}	50	4.07×10^{-7}
60	1.09×10^{-4}	60	1.62×10^{-6}
70	3.54×10^{-4}	70	4.49×10^{-6}

[a] $[M_1 + M_2] = 5.68 \times 10^{-1}$ mole/liter. $[M_1]/[M_2] = 1$. [AIBN] = 2.38×10^{-3} mole/liter.

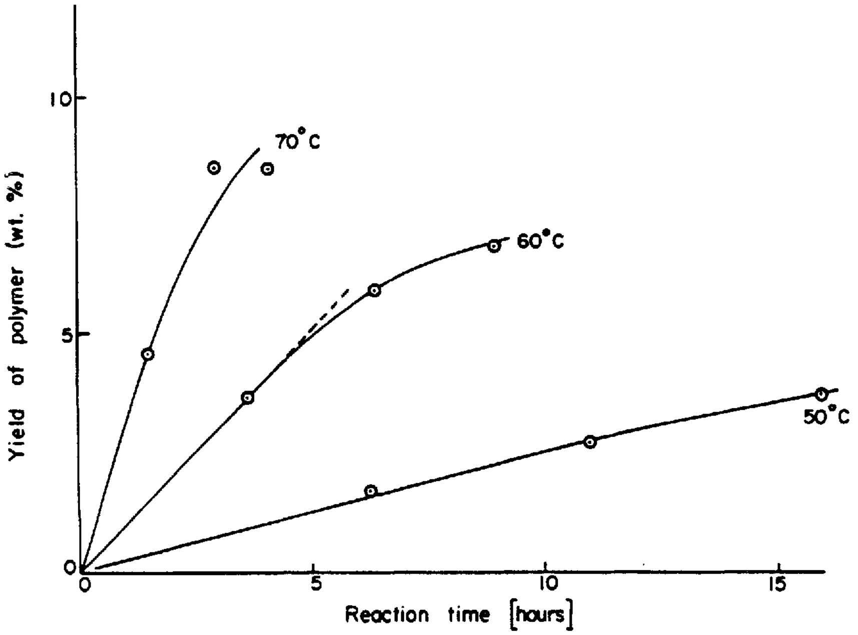


FIG. 9. Initial rate of copolymerization of MA-DVE in DMF. $[M_1 + M_2] = 5.68 \times 10^{-1}$ mole/liter, $[M_1]/[M_2] = 1$, [AIBN] = 2.38×10^{-3} mole/liter.

as much as 100-fold in $CHCl_3$ and in DMF. This can be explained by the great difference of dielectric constant and the powerful solvating ability of DMF which solvates the free monomer(s), preventing them from CT complexation.

The overall energy of activation, E_{act}, was calculated using the data in Table 4 by use of Arrhenius plots (Figs. 10 and 11). The values are shown in Table 5. Despite the great difference in solvating property of the solvent, the overall energy of activation obtained by this method was nearly the same in $CHCl_3$ and DMF. Since, in copolymerization, the expression of the overall rate of polymerization is very complicated, it is usually not possible to interpret and assign an activation energy to each elemental reaction. It appears, however, that the rate constants of initiation, propagation, and termination of this radical copolymerization may not be affected by

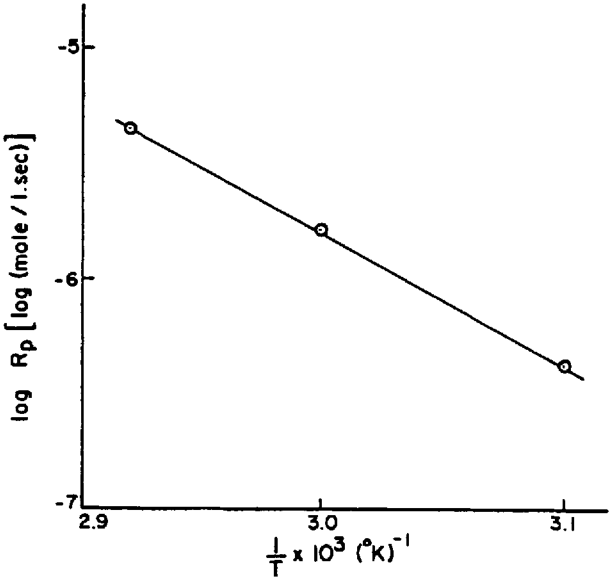


FIG. 10. Arrhenius plot of copolymerization of MA-DVE in $CHCl_3$. ΔE_{act} = 25.9 kcal/mole.

TABLE 5. Overall Energy of Activation of Copolymerization of MA-DVE[a]

Solvent	ΔE_{act} (kcal/mole)
$CHCl_3$	26.9
DMF	26.7

[a] $[M_1]/[M_2] = 1$. $[M_1 + M_2] = 5.68 \times 10^{-1}$ mole/liter. $[AIBN] = 2.28 \times 10^{-3}$ mole/liter.

the change in solvent; this is in agreement with the fact that the effect of solvent on the rate constant of radical reaction is generally very little [13].

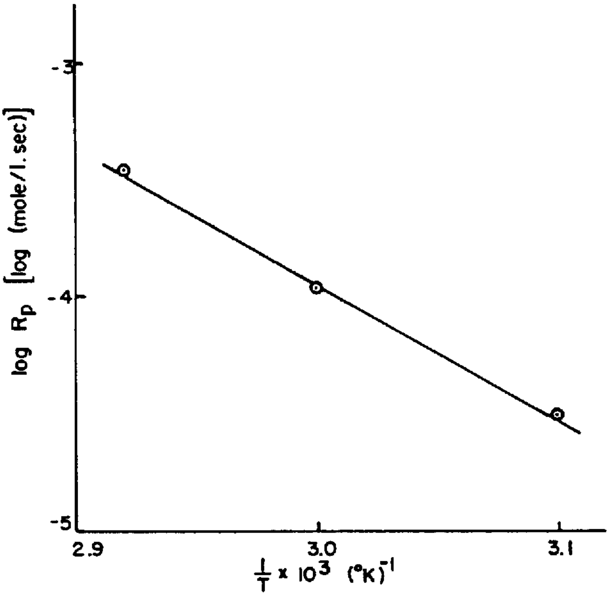


FIG. 11. Arrhenius plot of copolymerization of MA-DVE in DMF. ΔE_{act} = 26.7 kcal/mole.

The agreement of ΔE_{act} value in these solvents suggests that the equilibrium constant of complexation does not change independently in each solvent; that is, ΔH of CT complexation is small and approximately the same in both solvents [12]. This consideration of the overall energy of activation led to a study of spontaneous copolymerization of this system in $CHCl_3$ and CH_2Cl_2, which will be discussed later.

The number-average molecular weights of copolymer samples obtained in $CHCl_3$, as shown in Fig. 8, were measured and plotted as a function of conversion in Fig. 12. The molecular weight decreased with conversion since less monomer was available in the system at higher conversion. The molecular weight was lower at higher temperature because the thermal decomposition of AIBN is faster at the higher temperature. The results of Fig. 12 show that there was no living propagating species in the copolymerization.

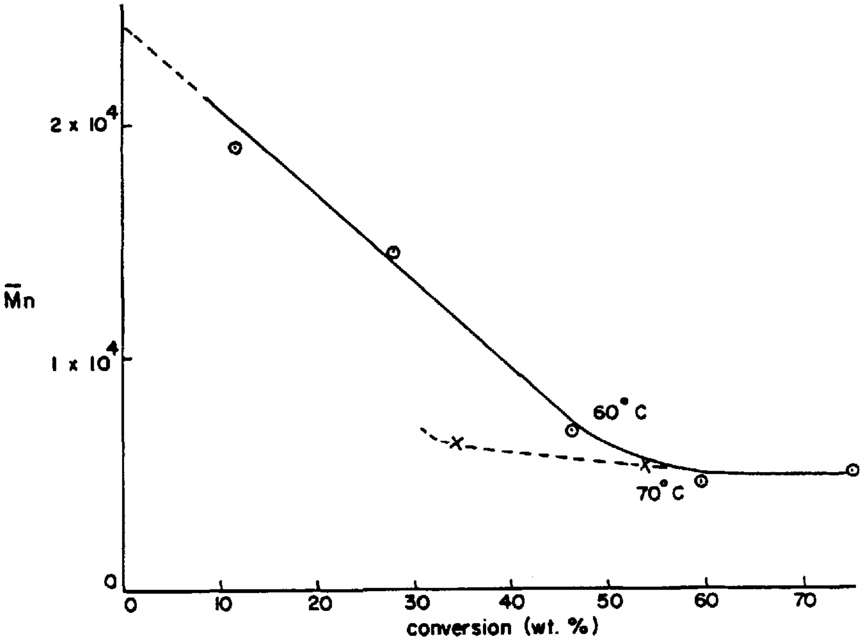


FIG. 12. Molecular weight vs conversion. Polymerization condition: $[M_1 + M_2] = 5.68 \times 10^{-1}$ mole/liter. $[M_1]/[M_2] = 1$, $[\text{AIBN}] = 2.38 \times 10^{-3}$ mole/liter.

INITIAL RATE OF COPOLYMERIZATION AS A FUNCTION OF FEED COMPOSITION

The initial rate of copolymerization was measured in $CHCl_3$ (dielectric constant = 4.806), CH_2Cl_2 (9.08) and DMF (37) as a function of feed composition.

$CHCl_3$ and CH_2Cl_2 were chosen to compare the initial rate because the measured equilibrium constant of complexation differed by a factor of 2 in these solvents as shown in Table 2, while the mode of solvation may not be drastically different because they are structurally similar. The polymerization was carried out under identical conditions. One sealed Pyrex tube was used for each feed composition. The polymerization was carried out in a thermostatted bath for a measured period of time and the reaction was stopped by immediately opening and pouring the contents into a large amount of nonsolvent. The yield was obtained by measuring the weight of polymer after purification. The results are shown in Fig. 13.

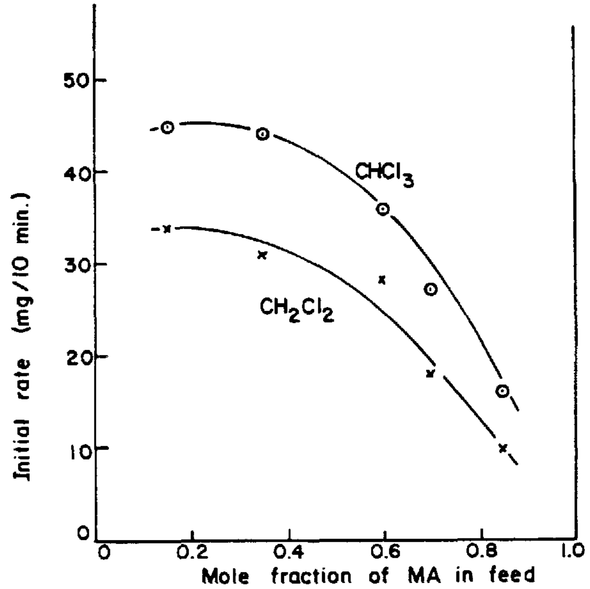
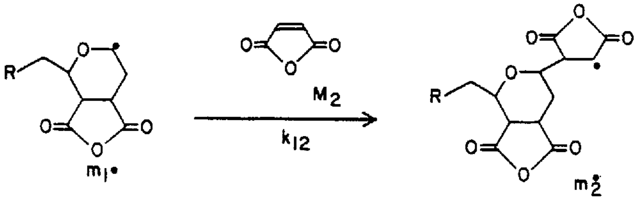


FIG. 13. Initial rate of copolymerization of MA-DVE as a function of feed composition. $[M_1 + M_2] = 5.68 \times 10^{-1}$ mole/liter, $[\mathrm{AIBN}] = 2.38 \times 10^{-3}$ mole/liter at 60°C.

Although the observed rate was not exactly proportional to the measured K-values in Table 2, the rate was much faster in $CHCl_3$ at all feed compositions, which is consistent with the higher K-value in $CHCl_3$. The measurements of equilibrium constants by both UV and NMR have inherent inaccuracies for complexes of this kind. In the Scott plot, the slope is very close to zero. A very small difference of slope or intercept results in a large change in the calculated K-value. Therefore this difference in initial rate in these solvents can be attributed to the different concentrations of the CT complex, which appears to be the polymerizing species.

The initial rate was also determined in DMF using a larger concentration of total monomers and AIBN. The results are shown in Fig. 14. It was significant that, under the conditions used for polymerization, the rate was faster in DVE-rich feed in all three solvents.

The kinetical derivation of the overall rate of copolymerization assuming the simplest propagation reactions [1], Eqs. (6) and (7), gives a rather complicated expression.



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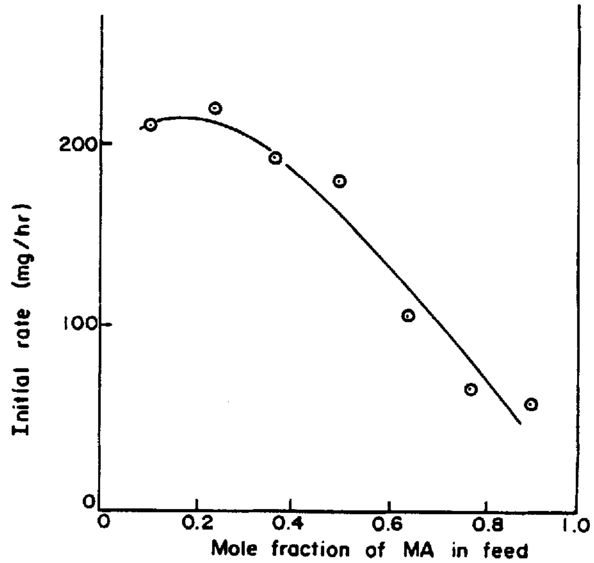
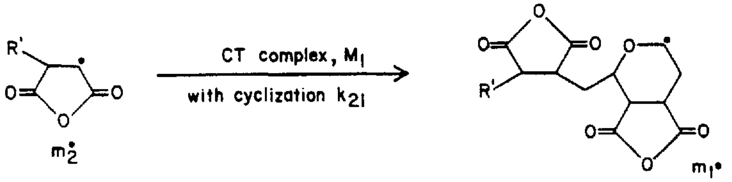


FIG. 14. Initial rate of copolymerization of MA-DVE in DMF as a function of feed composition. $[M_1 + M_2]$ = 1.28 mole/liter, [AIBN] = 6.10×10^{-2} mole/liter at 60°C.



(7)

$$R_p = \frac{2k_{12}k_{21}[M_1][M_2]R_i^{1/2}}{\left\{t_{11}(k_{21}[M_1])^2 + t_{22}(k_{12}[M_2])^2 + 2k_{12}k_{21}t_{12}[M_1][M_2]\right\}^{1/2}} \qquad (8)$$

where $R_i = k_d f[I_2]$ is rate of initiation, t_{11} and t_{22} are rate constants of termination of same type of radicals, t_{12} is the rate constant of cross-termination, $[M_1]$ and $[M_2]$ are concentrations of CT complex and MA, and k_{12} and k_{21} are rate constants of propagation as indicated in Eq. (6) and Eq. (7), respectively.

If cross-termination were the only termination reaction, a much simpler rate expression would be obtained for this scheme:

$$R_p = \left(\frac{2k_{12}k_{21}k_d f[I_2]}{t_{12}}\right)^{1/2} ([M_1][M_2])^{1/2} \qquad (9)$$

where $[M_1] \simeq K[MA][DVE]$. Therefore,

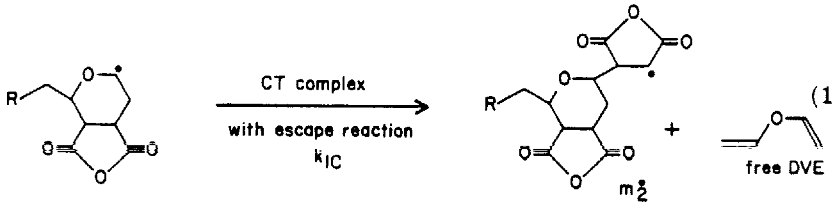
$$R_p = (\text{constants})^{1/2} \left(K \frac{[DVE]}{2}\right)^{1/2} [MA] \qquad (10)$$

Under these assumptions the overall energy of activation in Table 5 could be interpreted as a sum of enthalpies:

$$\Delta E_{act} = \frac{1}{2}(\Delta H_{CT} + \Delta H_{k_{21}} + \Delta H_{k_{12}} + \Delta H_{k_d} - \Delta H_{t_{21}}) \qquad (11)$$

Equation (10) predicts rate maximum at feed composition of 2:1 (= [MA]:[DVE]) and slower rate in DVE-rich feed.

If only the CT complex is assumed to be involved in the polymerization producing 2:1 (= MA:DVE) copolymer composition through the proposed "escape reaction," in which only one of the components of the CT complex reacts and the other "escapes" from reaction [14], the overall rate of copolymerization would be proportional to the concentration of the CT complex and the rate would be maximum at 1:1 feed composition (Eq. 14).



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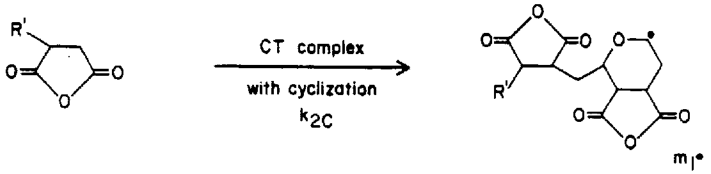

(13)

$$R_p = 2k_{2c}k_{1c}[C]\left(\frac{R_i}{t_{12}k_{1c}k_{2c} + t_{11}k_{2c}^{2} + t_{22}k_{1c}^{2}}\right)^{1/2} \qquad (14)$$

where $[C] \simeq K[MA][DVE]$.

If only cross-termination were the termination reaction, the overall energy of activation could be interpreted, under these assumptions, as

$$\Delta E_{act} = \Delta H_{CT} + \frac{1}{2}(\Delta H_{k_{2c}} + \Delta H_{k_{1c}} + \Delta H_{k_d} - \Delta H_{t_{12}}) \qquad (15)$$

The observed rate profile did not totally conform to either reaction scheme.

Number-average molecular weights and nitrogen contents, due mainly to AIBN fragments, were measured for the copolymers obtained in DMF. The results are plotted against feed composition in Fig. 15. The average molecular weight as measured by vapor pressure osmometry (VPO) was higher when the rate of polymerization was faster. The nitrogen content confirmed this trend. Since the rate of decomposition of AIBN is not altered by the feed composition [15], this shows that the kinetic chain length is larger in DVE-rich feed. Since the termination reaction does not change with feed composition, judging from the constant 2:1 copolymer composition, that is, the propagating radical is always the same, the longer kinetic chain length in DVE-rich feed means there is a greater chance of propagation in DVE-rich feed.

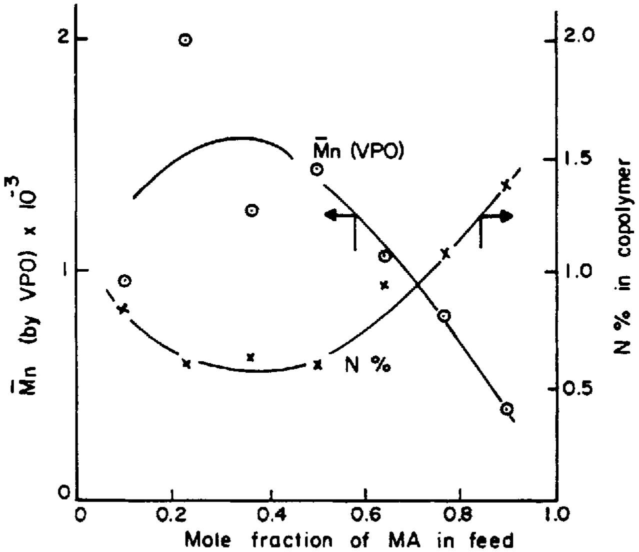

FIG. 15. Measured molecular weight by VPO and nitrogen content of copolymer of MA-DVE prepared in DMF; $[M_1 + M_2] = 1.28$ mole/liter, $[AIBN] = 6.10 \times 10^{-2}$ mole/liter at 60°C.

The measured number-average molecular weight by VPO did not agree with the calculated number-average molecular weight as determined by nitrogen content, assuming combination as the only termination reaction; $\overline{M}_n$ by VPO was much less. The NMR spectrum of copolymer prepared in DMF showed a very small amount of DMF tightly solvated to the copolymer even after five repeated purifications by dissolving the copolymer in acetone and precipitating into a large amount of boiling diethyl ether (Fig. 16). Since $\overline{M}_n$ measured by VPO will be very low when even a trace of low molecular weight impurity is present in the sample, the disagreement between the measured $\overline{M}_n$ by VPO and calculated $\overline{M}_n$ by nitrogen content could be due to the very small amount of tightly solvated DMF in the copolymer, which seemed impossible to separate [4, 16].

The NMR spectrum also confirmed the consumption of all the vinyl groups of the comonomers because only a negligible amount of vinyl proton absorptions could be seen.

The strong solvation of the copolymer suggests a pronounced effect of solvation of MA on the rate of polymerization, since MA is an extremely polar monomer. In DVE-rich feed, MA may be solvated by DVE molecules, eventually forming CT complex. The radical of MA ($m_2^{\cdot}$) could easily penetrate the solvent cage of the DVE molecules to polymerize the CT complex. But in MA-rich feed, the excess free MA may be tightly solvated by solvent, reducing the effective concentration of MA for CT complexation with DVE. The cyclized radical of DVE ($m_1^{\cdot}$) may not be able to easily penetrate the solvent cage around the MA molecule because of polar repulsions between the approaching $m_1^{\cdot}$ radical and polar groups of the solvating solvent, and between the MA unit of $m_1^{\cdot}$ radical and the MA molecule in the cage. This solvation effect of the solvent could be an explanation for the faster rate of propagation in DVE-rich feed and the slower rate in MA-rich feed. As a consequence, the position of maximum rate would have shifted toward DVE-rich feed in dilute systems.

The limiting conversion in different solvents, the results of which are shown in Table 6, may support this effect of solvation to MA. The conversion was measured after a long period of polymerization. If the copolymerization proceeds with consumption of MA and DVE in a 2:1 ratio, the limiting conversion will be the point where one of the comonomers has been completely consumed. When the initial comonomer ratio of [MA]/[DVE] in the feed = 1, the limiting conversion will be 79.2 wt%. In relatively poorly solvating $CHCl_3$ and CH_2Cl_2, the observed

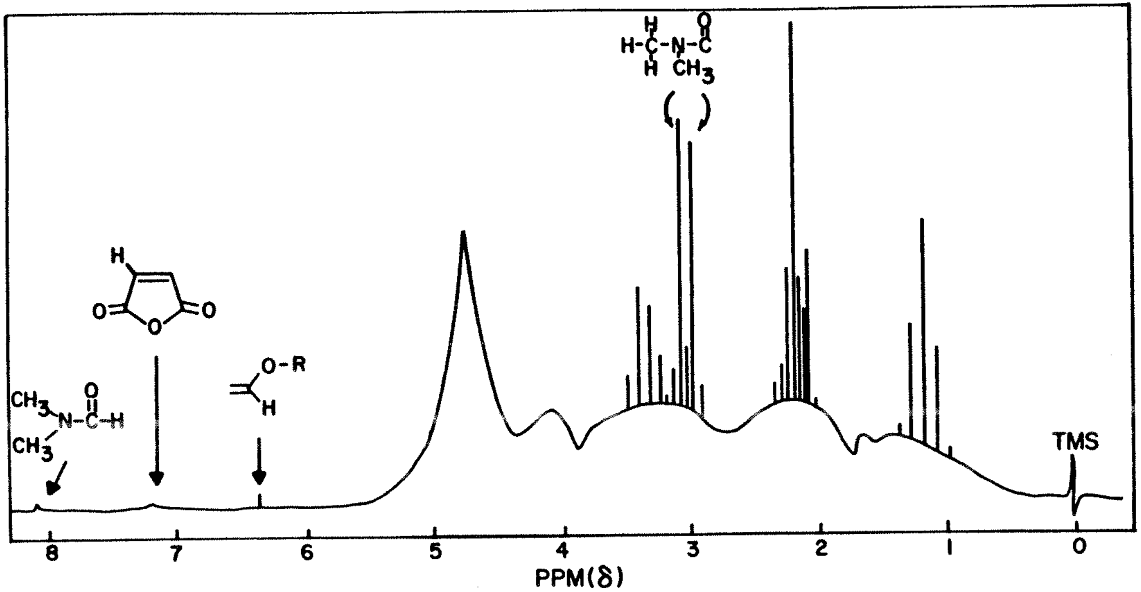

FIG. 16. NMR spectrum of copolymer of MA-DVE prepared in DMF (in deuterated acetone). Run No. M-D-9, $\overline{M}_n$ (VPO) = 410, N % = 1.38.

TABLE 6. Limiting Conversion of Copolymerization of MA-DVE[a]

Run	Solvent	Reaction time (hr)	Yield (wt%)
M-D-58	$CHCl_3$	24.0	75.7
M-D-55	CH_2Cl_2	24.3	79.6
M-D-60-55	DMF	73.5	26.7
Theoretical[b]	-	-	79.2

[a] $[M_1 + M_2] = 5.68 \times 10^{-1}$ mole/liter. $[M_1]/[M_2] = 1$, at 60°C. $[AIBN] = 2.38 \times 10^{-3}$ mole/liter.

[b] Perfect 1:2 consumption of comonomers was assumed.

values were in good agreement with the theoretical value, supporting the alternating structure of 2:1 composition of the copolymer. But in DMF, even less than half the theoretical conversion was obtained during a much longer period. These results suggest that DMF powerfully solvates the very polar MA molecule, preventing CT complexation with DVE. The MA may remain unattacked by the growing radical because it is strongly protected in the solvent cage.

Dead copolymer did not exert any significant effect as shown in Table 7. Only a slightly enhanced rate of copolymerization was observed; this was probably due to increased viscosity of the system which may have retarded the termination reaction.

Dependency of Rate of Copolymerization of Initiator Concentration

If the termination reaction is a bimolecular reaction, the overall rate of copolymerization should be proportional to one-half order of initiator concentration (Eq. 8 or Eq. 14). The rate of copolymerization was measured as a function of concentration of AIBN at 60°C in DMF. The results are shown in Fig. 17. One polymerization was carried out in a sealed tube for each AIBN concentration. The conversion of each run was below 10 wt%. The rate was closely proportional to one-half order of AIBN concentration, verifying the bimolecular termination reaction.

TABLE 7. Influence of Dead Polymer on Copolymerization of MA-DVE in DMF at 70°C[a]

Run	$\frac{[\text{Dead polymer}]}{[\text{MA monomer}]} \times 100$	Reaction time (hr)	Yield of new polymer (wt%)
M-D-70-52	0	3.0	8.5
DP-M-D-70-51	9.43	2.9	8.8
DP-M-D-70-52	27.5	2.9	8.8
DP-M-D-70-53	46.3	2.9	8.7

[a] $[M_1 + M_2] = 5.68 \times 10^{-1}$ mole/liter. $[M_1]/[M_2] = 1$. $[\text{AIBN}] = 2.38 \times 10^{-3}$ mole/liter. The same dead polymer was added to each run.

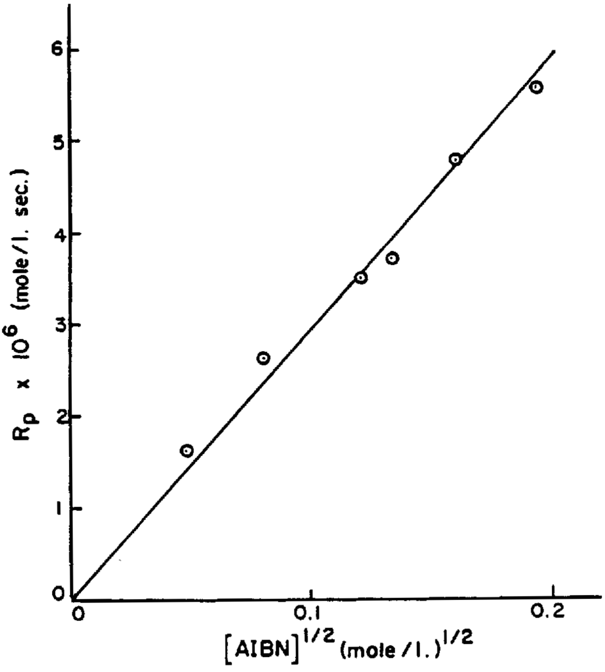

FIG. 17. Rate of copolymerization vs concentration of AIBN in DMF at 60°C. $[M_1]/[M_2] = 1$, $[M_1 + M_2] = 5.68 \times 10^{-1}$ mole/liter.

Charge-Transfer Polymerization

The energy diagram of the CT complex was proposed by Kosower [17]. The CT complex is predominantly in a no-bond state in the ground state of the complex. When energy is supplied, the complex will be excited to predominantly the dative state (Eq. 2) [5]. The thermal transition from the no-bond state to the dative state occurs at E_{Th} from the excited vibrational levels of the no-bond state, and λ_{max} shows the transition from the most populated vibrational level of the no-bond state of the complex. If enough energy is supplied, the dative state would be dissociated (Fig. 18). Since the dative state is charged, solvation and polarity of solvent stabilize the dative state

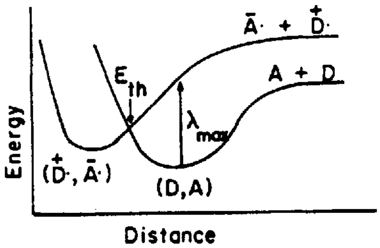

FIG. 18. Relationship between no-bond state and dative state of CT-complex.

more than the no-bond state and the energy of transition from the no-bond state to the dative state will be smaller (Fig. 19).

Spontaneous polymerization of donor-acceptor pairs has been known to be initiated either cationically or radically, or both [18, 19]. The dative state of the complex, which is formed by the thermal excitation of the vibrationally excited no-bond state, has been thought of as the initiating species. Therefore, when photoenergy is supplied to the system to bring the no-bond state to the dative state, initiation will be accomplished, [19] and the maximum rate of initiation could be expected at the wavelength of maximum CT transition (λ_{max}). Moreover, if higher energy is supplied to dissociate the dative state, such as γ-ray of ^{60}Co, initiation should be much easier.

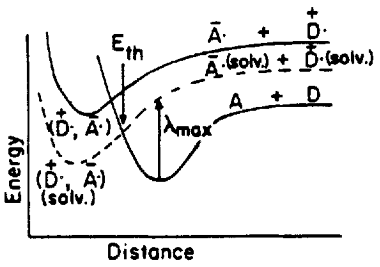

FIG. 19. Relationship between no-bond state and solvated dative state of CT-complex.

Thermal autopolymerization was carried out in bulk at 80°C in darkness. Photopolymerization was conducted in sealed Pyrex glass tubes using a Hanovia high-pressure UV lamp at room temperature. Although the Pyrex glass filters out UV radiation of shorter wavelength than 290 $m\mu$, the UV spectrum of the CT complex of the MA-DVE pair exhibits significant absorbance at wavelengths longer than 290 $m\mu$ (Fig. 1). Therefore, excitation of a portion of the no-bond state is still possible. High-energy polymerization was carried out in sealed Pyrex tubes continuously irradiated by γ-rays of a ^{60}Co source at room temperature. Although the amount of energy input was not measured in the photo- and γ-ray polymerizations, the energy supplied was the same in each run. Bulk polymerizations were carried out at a feed composition of $[MA]/[DVE] = 1/3$ and the preparation of the feed mixture was the same in all polymerizations. Extreme care was taken to avoid impurities.

The results of thermal autopolymerization, photopolymerization, and γ-ray polymerization are shown in Figs. 20, 21, and 22, respectively. Copolymerization occurred at a constant rate in each. In thermal autopolymerization, retardation was observed with hydroquinone. In addition, the structure and composition of the copolymers obtained in these three polymerizations were exactly the same as those of copolymers prepared with AIBN, judging from their IR spectra and hydrogen analyses. Although we did not investigate whether the dative state of the CT complex

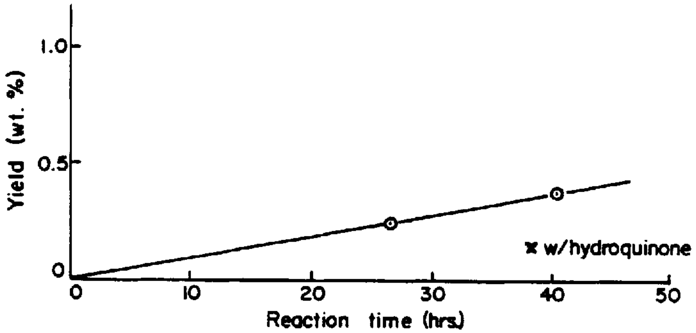

FIG. 20. Thermal autopolymerization of MA-DVE in dark. Bulk, at 80°C, $[MA]/[DVE] = 1/3$.

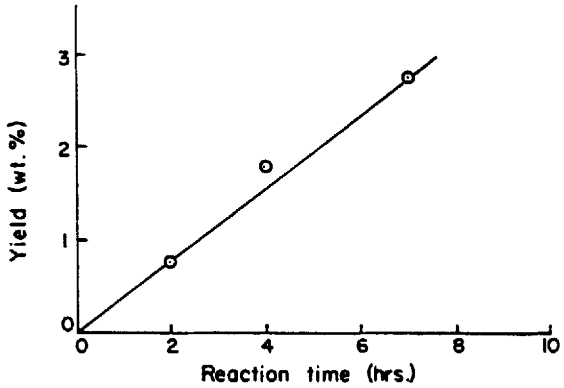

FIG. 21. Photopolymerization of MA-DVE in Pyrex glass tube. Bulk, at 24°C, [MA]/[DVE] = 1/3.

is the initiating species, in photopolymerization and γ-ray polymerization, respectively, since the monomers could be thermally excited to initiate polymerization, these observations suggest a radical mechanism for the copolymerization, at least in thermal autopolymerization. A more thorough examination is under way to determine whether or not the CT complex is the initiating species in photopolymerization [20].

Thermal Autopolymerization

It is very interesting to examine spontaneous polymerization of this system because the two factors involved can be separately observed; that is, the overall amount of CT complex which does not change significantly with temperature, [12] and the fraction of the dative state of the complex which depends on the population of vibrationally excited state of no-bond state of the CT complex, which, therefore, is significantly dependent on temperature (Figs. 18 and 19).

In the more polar solvent, K is smaller and the overall amount of CT complex is smaller. Therefore, the rate of propagation will be less. In more polar solvent, however, the fraction of dative state, which is a charged state, will be larger since it is better

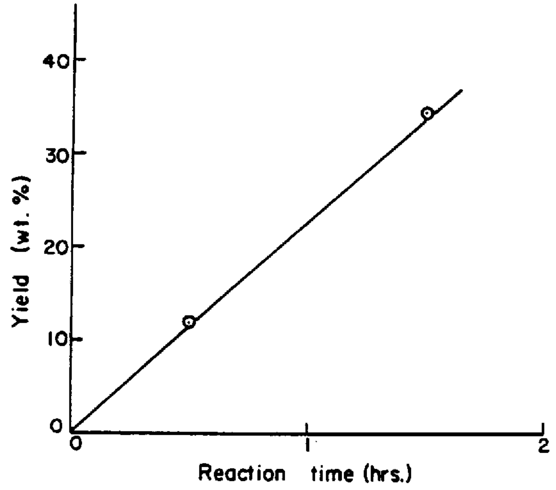

FIG. 22. γ-Ray polymerization of MA-DVE. Bulk, at 25°C, [MA]/[DVE] = 1/3.

stabilized by the polar solvent and therefore a larger rate of initiation would be expected. Of course, in the ground state the amount of the dative state is very small compared with the amount of the CT complex itself.

Chloroform (dielectric constant = 4.806, $K^{24°C} = 3.6 \times 10^{-2}$) and methylene chloride (dielectric constant = 9.08, $K^{38°C} = 1.4 \times 10^{-2}$) were chosen here as the solvents to compare the thermal autopolymerization because these polyhalomethanes may not be greatly different in solvation behavior, but have a twofold difference in dielectric constant. The results are shown in Fig. 23, and may be explained as follows: At 50°C the amount of the dative state was very small in both solvents but much more in polar CH_2Cl_2 than in $CHCl_3$. Initiation seemed to be more important than propagation. Thus the rate reflected the difference in the amount of initiating species and was faster in CH_2Cl_2. But at 70°C, vibrational excitation from the no-bond state of the complex to the dative state occurred much more frequently and there was relatively more dative state in both solvents than at 50°C. The amount of initiation species was not so greatly different and was no longer the controlling

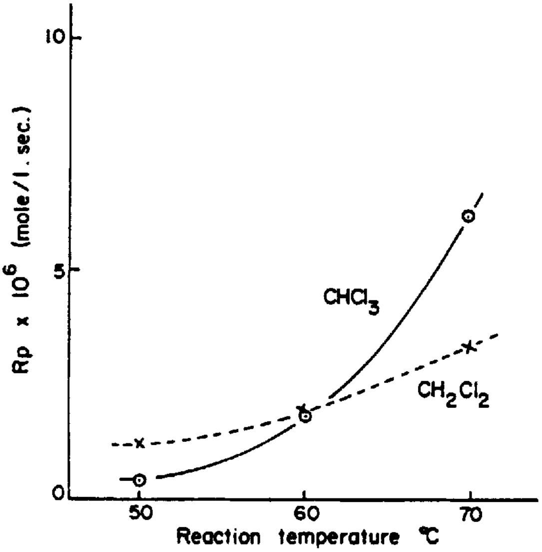

FIG. 23. Initial rate of spontaneous copolymerization of MA-DVE. $[M_1 + M_2] = 5.68 \times 10^{-1}$ mole/liter, $[M_1]/[M_2] = 1$.

factor, but it was the amount of overall CT complex which played a role in the propagation that made the difference in rate. Thus the rate was faster in the less polar $CHCl_3$ in which there was more CT complex for the propagation reaction. Hence the cross-over in the rate-temperature plot of the spontaneous copolymerization which was observed may be explained on this basis.

EXPERIMENTAL

Materials

Maleic anhydride was recrystallized from benzene and sublimed before use. Divinyl ether (Merck, Sharp and Dohme) was distilled before use. Reagent grade solvents were used as received. Azobisisobutyronitrile (AIBN) was recrystallized from methanol.

Polymerization

MA and AIBN were weighed and dissolved in the solvent in volumetric flasks. DVE was measured volumetrically and dissolved in the solvent in a volumetric flask. The solutions were transferred to Pyrex glass tubes. The content of the tubes was frozen with liquid nitrogen and the tubes were evacuated. The freeze-thaw cycle was repeated twice on a vacuum line under a pressure of 10^{-5} Torr or better and the tubes were sealed. The polymerizations were carried out in a thermostatted oil bath with temperature controlled within ±0.01°C. The polymer was purified by dissolving in acetone and precipitating with anhydrous diethyl ether. This procedure was repeated three times. The precipitated polymer was filtered and dried in a vacuum oven at about 40°C before analysis.

The spontaneous polymerizations were carried out in Pyrex glass tubes. Freshly sublimed MA was weighed into flamed tubes. DVE was dried over sodium sulfate overnight and distilled through the vacuum line into the polymerization tubes. The polymerization tubes were cleaned with a chromic acid mixture, washed with tap water vigorously, and then with steam for half an hour before use. A Hanovia high pressure UV lamp and a ^{60}Co γ-ray source of the University of Florida were used for photo- and γ-ray polymerizations, respectively.

Analysis

Copolymer composition was calculated from high-frequency titration results of the MA unit with aqueous NaOH solution and HCl solution, using a Sargent Chemical Oscillometer, Model V. The elemental analyses were done by PCR, Inc., Gainesville, Florida. Number-average molecular weights were measured in acetone solution by use of a Mechrolab Vapor Pressure Osmometer, Model 302.

Determination of Equilibrium Constant of Complexation

A Beckman DK-2A Spectrophotometer was used for the spectrophotometric studies of complexation. The spectra were taken using the same concentration of donor compound in the sample cell and in the reference cell, and a constant small concentration of MA in the sample cell. Thus the absorption of the donor was subtracted by the reference solution. The absorption of the CT complex was obtained by subtracting the absorption of MA numerically. A Varian Associates analytical NMR spectrometer, Model A-60 was used for the NMR studies. Spectrograde solvents were used for the complex studies.

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