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Studies in Cyclocopolymerization. XI. The Role of the Charge-Transfer Complex in the Initiation Step of the UV-Initiated Cyclocopolymerization of Divinyl Ether with Fumaronitrile*

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ABSTRACT

A soluble cyclocopolymer of 1:2 composition was obtained by UV irradiation of divinyl ether (DVE) and fumaronitrile (FN) in methanolic solution. By appropriate calculations based on the results of the rate observed under different concentration conditions and with different UV filters, it is shown that both the complex formed between DVE and FN, and the noncomplexed species (DVE, FN, and methanol) are able to initiate the polymerization by light excitation. A study was completed on the same polymerization in the same solvent initiated by a radical initiator. The characteristics of the polymers are the same as those of the photoinitiated polymers. The kinetic results are similar when the polymers are obtained by both kinds of initiation, indicating a similar polymerization mechanism.

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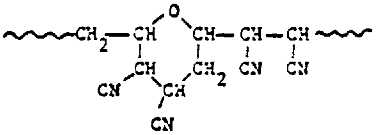
INTRODUCTION

In several previous papers [1-4] it has been shown that certain 1,4-dienes and monoolefins of different polarity, which form charge-transfer (C.T.) complexes, copolymerize easily, leading to soluble copolymers. The composition of the copolymer is diene/monoolefin = 1/2 when the monomers are not able to homopolymerize as in the case of the divinyl ether (DVE)-fumaronitrile (FN) system. A cyclic structure has been assigned:



All the polymerizations described in previous papers were initiated by radical initiators. In order to elucidate the mechanism of initiation and to discuss the role of the C.T. complex, it was decided to photoinitiate one of the systems previously studied. The DVE-FN system in methanol was chosen because the absorptions of the complex and the noncomplexed species are well separated, as shown in the study of the complex (Fig. 2).

On the basis that the concentration of excited-state species which are able to initiate the polymerization depends on the number of photons absorbed by the solution and on the quantum yield at each wavelength, it was decided to change the intensity of the incident light and its wavelength (for this, different UV filters were used), and/or to change the concentration of the monomers. An appropriate method of calculation is developed and the rate of polymerization is correlated with the total number of photons absorbed by the complex and the noncomplexed species (DVE, FN, and methanol) and with the quantum yield of the polymerization.

The same polymerization in the same solvent was also studied when initiated by a radical initiator (AIBN). Comparison between the results obtained by the two modes of initiation was of considerable interest.

EXPERIMENTAL

DVE (Merck, Sharp and Dohme) was distilled at 28-29°C. FN (Aldrich Chemical Co.) was recrystallized from benzene solution. Spectrophotometric methanol (J. T. Baker Chem. Co.) was used.

AIBN was recrystallized from methanol. Reagent grade chemicals were used for the actinometry: Potassium oxalate.H_2O (Fisher Scientific Co.); Ferric sulfate.$7H_2O$ (J. T. Baker Chemical Co.); 1.10-phenanthroline (Fisher Scientific Co.); sodium acetate (Fisher Scientific Co.); ferric chloride (Allied Chemical).

The UV study was carried out with a Beckman DK-2A spectrophotometer at 23°C, in methanol, with 1 cm cells. For the study of pure DVE or FN, pure methanol was used as reference. For the study of the complex, the reference cell was filled with FN in methanol at the same concentration as in the complex solution cell and the optical density of pure DVE at the same concentration was deducted from the optical density measured because DVE and FN present some residual absorption below 300-320 mμ. The exact value of the optical density of the complex can thus be evaluated.

IR spectra were recorded on a Perkin Elmer (Infracord) spectrophotometer. Molecular weights were determined by a vapor pressure osmometer, Mechrolab Model 302. Elemental analyses were carried out by Galbraith Laboratories, Inc.

A rough draft of the irradiation apparatus is given in Fig. 1. A methanolic solution (5 ml) was contained in a quartz polymerization tube, a (radius = 1.1 cm). Polymerizations were carried out under high vacuum. During polymerization, the tube was slowly rotated. The temperature of the solution varied between 26 and 28°C. Concentrations of DVE and FN were 0.6, 0.9, or 1.2 moles/liter. A filter b held by a filter holder c was positioned in front of the solution. Interference filters at 2537 and 2000 Å were used (Oriel Optics Corporation Catalog Nos. G-571-2537 and G-572-2000). The other filters are simple UV filters from Corning Glass Works (Catalog Nos. 954, 930, 054, 053, and 052). Transmittances of all these filters vs the wavelength are given in Fig. 7. To avoid any kind of interaction of DVE in the vapor phase with the light, an aluminum sheet d was placed around the tube, and a screen e was placed between the lamp and the tube. A Hanovia high-pressure mercury lamp f (450 W; Catalog No. 679 A-36), strongly cooled by a fan, was employed as the light source. The power of the lamp for each mercury line is given in Table 2. The distance between the lamp and the polymerization tube was 2 cm. The top of the quartz polymerization tube is sealed to a Pyrex tube obtained from Lab Glass Inc. (Catalog No. LG-10861). The sealing of the tube under high vacuum after successive degasifications was always carried out at the level of the Pyrex part h.

AIBN-initiated polymerization was also carried out under high vacuum after successive degasifications at 60°C in an oil bath.

The polymers obtained by UV initiation as well as by radical initiation were directly filtered and washed several times by boilmethanol. The rate of polymerization was measured by gravimetry after drying the polymers several hours under vacuum at 40°C.

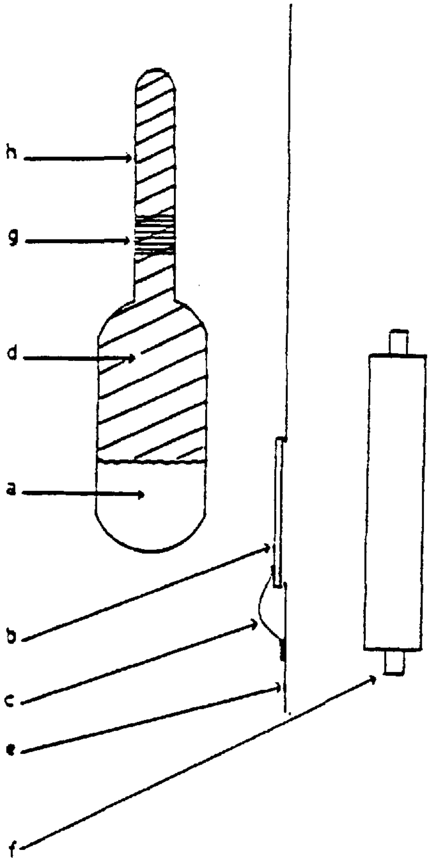


FIG. 1. Rough draft of the irradiation apparatus. a = solution in a quartz tube; b = filter; c = filter holder; d = aluminum sheet; e = screen; f = UV lamp; g = seal of quartz tube to Pyrex tube; h = Pyrex tube.

Study of the DVE-FN Complex in Methanol

On the basis that the complex formed between DVE and FN may participate in the mechanism of initiation of the photopolymerization in methanolic solution, the characteristics of the complex were studied in the same solvent. The existence of the complex was established by UV spectrophotometry: a mixture of DVE and FN shows a new absorption band (Fig. 2); $\lambda_{max} \simeq 260$ mμ. A 1:1 stoichiometry

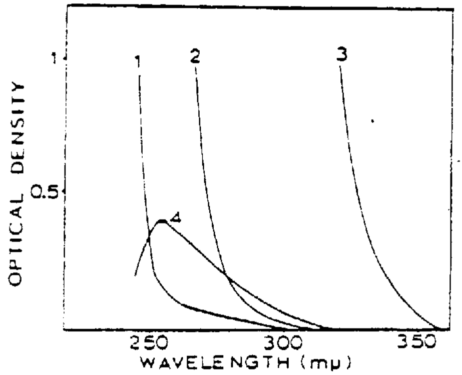


FIG. 2. Identification of the DVE-FN complex in methanol. (1) DVE at 0.6 mole/liter: (2) FN at 0.6 mole/liter; (3) DVE + FN at 0.6 mole/liter; (4) DVE + FN at 0.06 mole/liter.

was determined by the continuous variations method [5]; indeed, the maximum of the optical density for different compositions of DVE and FN, while their total concentration was kept constant, was found for equimolar fractions (Fig. 3). Finally, the equilibrium constant of the complex formation was determined by the Benesi-Hildebrand method [6]; even though different concentration conditions and

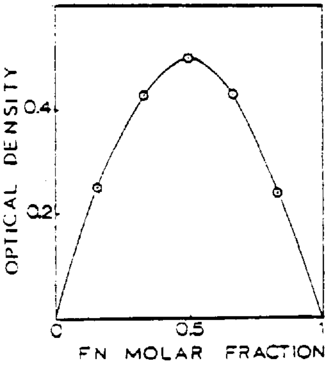


FIG. 3. Determination of the stoichiometry of the DVE-FN complex in methanol by the continuous variations method. Optical density at 260 mμ. (DVE) + (FN) = 0.15 mole/liter.

different wavelengths were used, it appears that value of the equilibrium constant is small and cannot be evaluated exactly: 0 > K > 0.20 (Fig. 4). Values of 0.015 in methylene chloride [3] and 0.008 in deuterochloroform [4] were reported earlier. However, the present approximation is sufficient for our study as explained further.

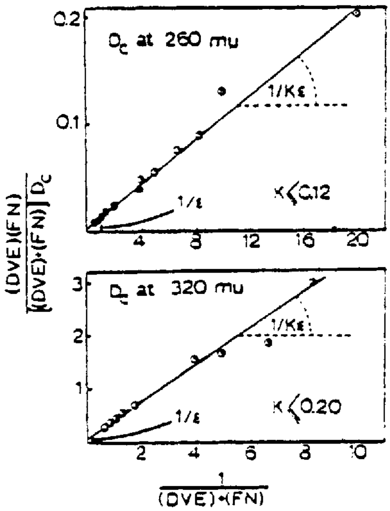


FIG. 4. Determination of the equilibrium constant of the DVE-FN complex in methanol solution by Benesi-Hildebrand's method at two different wavelengths and different concentration conditions. (⊙) (DVE) = (FN); (●) (FN) = 0.005 mole/liter ≪ (DVE).

Copolymerization of DVE-FN Initiated by AIBN

The copolymerization of DVE-FN in methanol at 60° C and initiated by AIBN was studied in order to compare the results obtained in the photopolymerization of the same system in the same solvent. To get the most valid comparison, concentrations and compositions of DVE and FN were the same, and the AIBN concentration was chosen so that the rate of polymerization lies in the same range of magnitude as the rate observed in the photopolymerization. First of all, one observes that the molar fraction of FN in the copolymers is approximately 0.59-0.62; this fraction is close to the 1:2 composition as indicated earlier.

Essentially, the dependencies of the monomers and AIBN

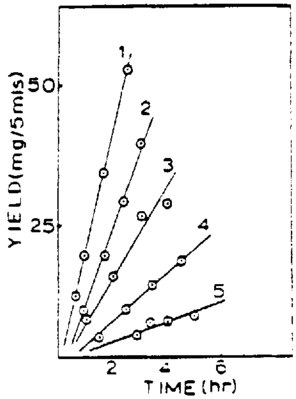


FIG. 5. Initial rate of DVE-FN copolymerization in methanol at 60°C initiated by AIBN. (1) (DVE) = (FN) 1.2 mole/liter, (AIBN) = 6×10^{-3} mole/liter; (2) (DVE) = (FN) = 0.9 mole/liter, (AIBN) = 6×10^{-3} mole/liter; (3) (DVE) = (FN) = 0.6 mole/liter, (AIBN) = 6×10^{-3} mole/liter; (4) (DVE) = (FN) = 0.6 mole/liter, (AIBN) = 3×10 mole/liter; and (5) (DVE) = (FN) = 0.6 mole/liter, (AIBN) = 1.2×10^{-3} mole/liter.

concentrations on the rate of polymerization were studied. The yields observed were plotted vs time (Fig. 5) in order to determine accurately the rate of polymerization under the different concentration conditions (Table 1). The slope of the plot of log rate vs log monomer or AIBN concentration (Fig. 6) gives the order of polymerization. An order 1.5 and 1 for the total monomer concentration and for the AIBN concentration, respectively, were found so that the rate can be expressed by

$$\text{rate} = k[(\text{DVE}) + (\text{FN})]^{1.5}(\text{AIBN}) \qquad (1)$$

The exact nature of the order 1.5 for the total monomer concentration is discussed in another paper [7] in the case of the copolymerizations of divinyl ether-maleic anhydride and ethyl vinyl ether-maleic anhydride. The order 1 for the AIBN concentration indicates that the termination of the growing radicals is not a termination by coupling. This order is strongly supported by the fact that the molecular weights of the polymers remain constant for different AIBN concentrations (Table 1).

TABLE 1. Summary of the Results of the DVE-FN Copolymerization in Methanol at 60°C Initiated by AIBN

(AIBN) (moles/liter × 10^3)	(DVE) + (FN) m/l	m_{FN}[a]	MW	Rate (mg/5 ml, liter/sec)
1.2	1.2	0.61	3200	4.44×10^{-4}
3	1.2	0.62	3200	11.3×10^{-4}
6	1.2	0.59	3600	24.3×10^{-4}
6	1.8	0.605	-	40.3×10^{-4}
6	2.4	0.62	-	65.3×10^{-4}

[a] Calculated from nitrogen analysis. The values are mean values from different samples.

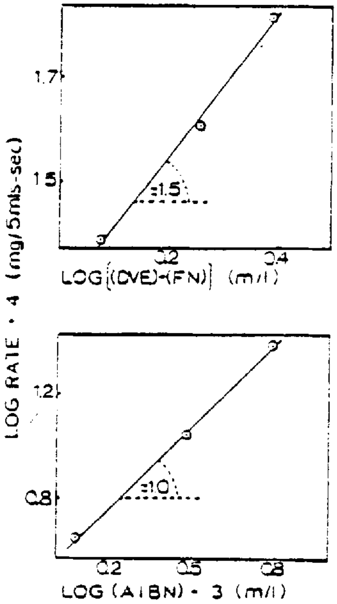


FIG. 6. Dependence of the monomer concentration and the AIBN concentration on the rate of polymerization.

Determination of the Number of Photons Absorbed

According to Beer's law, the number of photons, $(N_{abs,T})_{\Delta\lambda}$, absorbed by the solution per second in a wavelength range $\Delta\lambda$ is

$$(N_{abs,T})_{\Delta\lambda} = (N_0)_{\Delta\lambda}\,(10^{D_\lambda} - 1/10^{D_\lambda}) \tag{2}$$

$(N_0)_{\Delta\lambda}$ is the number of incident photons per second in $\Delta\lambda$, and D_λ is the optical density of the solution at wavelength $(\lambda_2 + \lambda_1)/2$ ($\Delta\lambda = \lambda_2 - \lambda_1$). From the design of the apparatus, $(N_0)_{\Delta\lambda}$ can be determined by

$$(N_0)_{\Delta\lambda} = (N_L)_{\Delta\lambda}\,\alpha\,(T_F)_\lambda (T_Q)_\lambda \tag{3}$$

where $(N_L)_{\Delta\lambda}$ is the number of photons emitted by the lamp per second in the range $\Delta\lambda$; α is a factor involving the geometry of the apparatus (distance, cross area of the solution); and $(T_F)_\lambda$ and $(T_Q)_\lambda$ are, respectively, the transmittance of the filter and the quartz tube at a wavelength $(\lambda_2 + \lambda_1)/2$. Combining Eqs. (1) and (2):

$$(N_{abs,T})_{\Delta\lambda} = \alpha (N_L)_{\Delta\lambda} (T_F)_\lambda (T_Q)_\lambda (10^{D_\lambda} - 1/10^{D_\lambda}) \tag{4}$$

The fraction of $(N_{abs,T})_{\Delta\lambda}$ absorbed by the noncomplex (NC) species (DVE + FN + methanol) and the complex (C) are $(N_{abs,NC})_{\Delta\lambda}$ and $(N_{abs,C})_{\Delta\lambda}$, respectively:

$$(N_{abs,NC})_{\Delta\lambda} = (N_{abs,T})_{\Delta\lambda}\,\frac{(\epsilon_\lambda c)_{NC}}{(\epsilon_\lambda c)_{NC} + (\epsilon_\lambda c)_C}$$

$$(N_{abs,C})_{\Delta\lambda} = (N_{abs,T})_{\Delta\lambda}\,\frac{(\epsilon_\lambda c)_C}{(\epsilon_\lambda c)_{NC} + (\epsilon_\lambda c)_C}$$

and

$$(N_{abs,T})_{\Delta\lambda} = (N_{abs,NC})_{\Delta\lambda} + (N_{abs,C})_{\Delta\lambda} \tag{5}$$

where $(\epsilon_\lambda c)_{NC}$ and $(\epsilon_\lambda c)_C$ correspond to the absorbance (for a cell of 1 cm) at $(\lambda_2 + \lambda_1)/2$ of the noncomplex species and the complex, respectively. All these equations are established for a wavelength range $\Delta\lambda$. The summation of all the terms involved in relation (5) over the spectrum leads to the total number of photons absorbed per second by the whole solution, the noncomplex species, and the complex; we note these values $N_{abs,T}$, $N_{abs,NC}$, and $N_{abs,C}$:

$$\begin{aligned} N_{abs,T} &= \Sigma(N_{abs,T})_{\Delta\lambda} \\ &= \Sigma(N_{abs,NC})_{\Delta\lambda} + \Sigma(N_{abs,C})_{\Delta\lambda} \\ &= N_{abs,NC} + N_{abs,C} \end{aligned} \tag{6}$$

The determination of the different parameters entering into the above relations are considered further here.

The number of photons $(N_L)_{\Delta\lambda}$ emitted by the lamp per second in a wavelength range $\Delta\lambda$ is equal to the power of the lamp $P_{\Delta\lambda}$ in the same $\Delta\lambda$ divided by the energy of one photon hc/λ:

$$(N_L) = P_{\Delta\lambda}\lambda/hc \tag{7}$$

If $P_{\Delta\lambda}$ is given in watts (J/sec) and λ in Å, then

$$(N_L)_{\Delta\lambda} = P_{\Delta\lambda}\lambda\, 5.02 \times 10^{14} \tag{8}$$

The values of $P_{\Delta\lambda}$ for each mercury line of the lamp and the associate values of $(N_L)_{\Delta\lambda}$ are given in Table 2. Using this manner of calculation, one observes that $\Delta\lambda$ is not constant. However, the calculations are not affected if $\Delta\lambda$ represents the width of each of the emission lines of the lamp since the output of the lamp between the lines is practically zero. In regard to this remark, it is quite evident that the values of $(T_F)_\lambda$, $(T_Q)_\lambda$, D_λ, $(\epsilon_\lambda c)_{NC}$, and $(\epsilon_\lambda c)_C$ are taken at the λ_{max} of the emission lines.

The parameters $(T_F)_\lambda$ and $(T_Q)_\lambda$ are directly determined by UV spectroscopy or are available from the technical data sheets. Figure 7 represents the transmittances observed.

TABLE 2. Power of the Lamp and Number of Photons Emitted by the Lamp for the Different Emission Lines

λ (Å)	$P_{\Delta\lambda}$ (W)	$(N_L)_{\Delta\lambda}$ (sec^{-1}) (10^{-18})
3660	25.6	47.0
3340	2.4	4.02
3130	13.2	20.7
3020	7.2	10.9
2970	4.3	6.41
2890	1.6	2.31
2800	2.4	2.87
2750	0.7	0.96
2700	1.0	1.35
2650	4.0	5.32
2570	1.5	1.93
2540	5.8	7.39
2480	2.3	2.86
2400	1.9	2.29
2380	2.3	2.74
2360	2.3	2.72
2320	1.5	1.75
2220	3.7	4.12

The parameter $(10^{D_\lambda} - 1)/10^{D_\lambda}$ was determined as follows:

$$D_\lambda = [(\epsilon_\lambda c)_{NC} + (\epsilon_\lambda c)_C]d \tag{9}$$

According to Beer's law in which D_λ is the optical density of the solution in the polymerization vessel, d is the thickness of the polymerization vessel, and $(\epsilon_\lambda c)_{NC}$ and $(\epsilon_\lambda c)_C$ are the optical densities of the

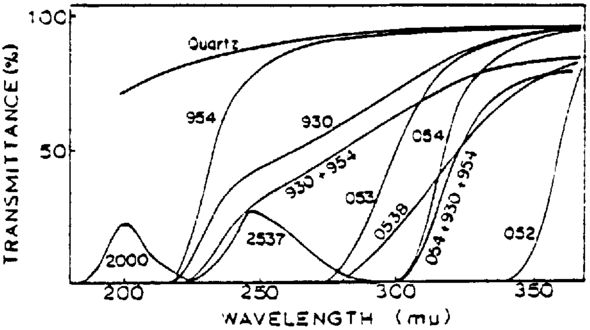


FIG. 7. Transmittance of the filters vs the wavelength. The numbers refer to the catalog numbers of the filters.

noncomplexed species (DVE + FN + methanol) and the complex, respectively, in a 1 cm cell. Knowing the different values of the optical densities in relation (9) (see further), the value of $(10^{D\lambda} - 1)/10^{D\lambda}$ would have been easily determined if a square cell had been used as the polymerization vessel. However, since a tube was used, d takes different values at the different positions in the tube so that a mean value of $(10^{D\lambda} - 1)/10^{D\lambda}$ must be calculated. However, the integrals of $(10^{D\lambda} - 1)/10^{D\lambda}$ for continuous variations of d from 0 to the diameter of the tube do not offer a direct solution. The problem was solved by computer calculation, the details of which are given in the Appendix. The values found vs the wavelength are presented in Fig. 8 for concentration (DVE) = (FN) = 0.6 mole/liter. Similar figures might be drawn for the other concentrations.

The parameter $(\epsilon_\lambda c)_{NC}$ was determined as follows. The values of the optical densities (in a 1-cm cell) of the methanol, and those of DVE and FN in methanolic solution at the same concentrations as used in the polymerization (0.6, 0.9, and 1.2 moles/liter), were directly measured by UV spectrophotometry when they are higher than 0.01 and lower than 2 (limits of the Beckman DK-2A spectrophotometer). Otherwise they were calculated following Beer's law from the data obtained at more concentrated or more dilute solutions. Figure 9 represents the optical densities at one of these concentrations. The sum of these values gives the optical density of all the noncomplexed species.

The parameter $(\epsilon_\lambda c)_C$ was determined as follows. Above 330 mμ the optical density (in a 1-cm cell) of the complex DVE-FN, $(\epsilon_\lambda c)_C$,

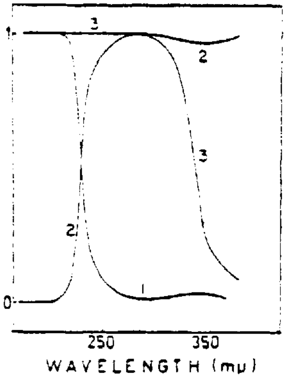


FIG. 8. $(\epsilon_{\lambda}c)_{NC}/[(\epsilon_{\lambda}c)_{NC} + (\epsilon_{\lambda}c)_{C}]$ (1), $(\epsilon_{\lambda}c)_{C}/[(\epsilon_{\lambda}c)_{NC} + (\epsilon_{\lambda}c)_{C}]$ (2), and $(10^{D\lambda} - 1)/10^{D\lambda}$ (3) vs wavelength for (DVE) = (FN) = 0.6 mole/liter.

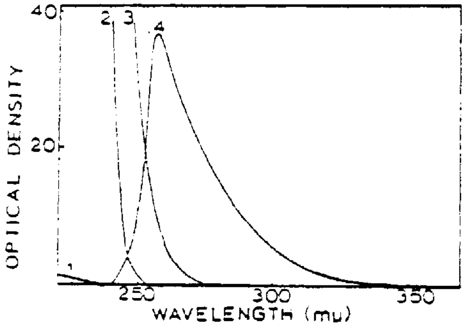


FIG. 9. Optical density observed or calculated vs wavelength. (1) Pure methanol; (2) DVE at 0.6 mole/liter in methanol; (3) FN at 0.6 mole/liter in methanol; and (4) DVE + FN at 0.6 mole/liter in methanol calculated for an equilibrium constant of complexation approaching 0. The same kind of curves can be obtained for other concentrations.

at concentrations in DVE and FN equal to 0.6, 0.9, and 1.2 moles/liter, was directly measured. For lower wavelengths the optical density was measured at concentrations (DVE) = (FN) = 0.06 mole/liter, and then recalculated from the value of the equilibrium constant for the concentrations 0.6, 0.9, and 1.2 moles/liter. It has been shown in the study of the complex that the equilibrium constant K is higher than 0 but lower than 0.2. If K is very low the concentration of the complex increases 100, 225, and 400 times when the concentration of each component increases from 0.06 to 0.6, 0.9, and 1.2 moles/liter, respectively. If K = 0.2 these increase factors are approximately 85, 191, and 340, respectively. Thus the optical densities of the complex for concentrations in DVE and FN equal to 0.6, 0.9, and 1.2 moles/liter are, respectively, 100, 225, and 400 times, or 85, 191, and 340 times higher than the optical densities measured for (DVE) = (FN) = 0.06 mole/liter following $K \to 0$ or K = 0.2. However, the general trend of further calculations is practically not affected when $(\epsilon_\lambda c)_C$ is evaluated with multiplication factors 100, 225, and 400, or 85, 191, and 340. Indeed: 1) Up to 330 mμ the optical densities are so high that small variations of $(\epsilon_\lambda c)_C$ cannot affect the value of $(10^{D_\lambda} - 1)/10^{D_\lambda}$ which shows a constant value equal to one (Fig. 8). 2) It can be observed in Fig. 8 that the ratios

$$\frac{(\epsilon_\lambda c)_{NC}}{(\epsilon_\lambda c)_{NC} + (\epsilon_\lambda c)_C}$$

and

$$\frac{(\epsilon_\lambda c)_C}{(\epsilon_\lambda c)_{NC} + (\epsilon_\lambda c)_C}$$

take the values of 1 or 0 (except in a transition wavelength region at approximately 250 mμ). This means that the absorption of the solution is either due to the noncomplexed species or to the complex depending on the wavelength. Therefore, small variations of $(\epsilon_\lambda c)_C$ cannot greatly affect the values of these ratios. The optical density of the complex at concentrations (DVE) = (FN) = 0.6 mole/liter calculated with $K \to 0$ is represented in Fig. 9.

The factor α was determined by the actinometric method described by Hatchard and Parker [8]. Potassium ferrioxalate (5 ml) at 0.006 mole/liter was irradiated under exactly the same conditions as in the photopolymerization with the interference filter 2537.

The concentration of Fe(II) after different times of irradiation was determined by measuring the optical density (at 510 mμ) of the complex formed with 1,10-phenanthroline. The plot of optical density vs time (Fig. 10) gives the rate of increase of optical density: 15.4×10^{-3} sec^{-1}. From the extinction coefficient of the complex Fe(II)-1,10-phenanthroline

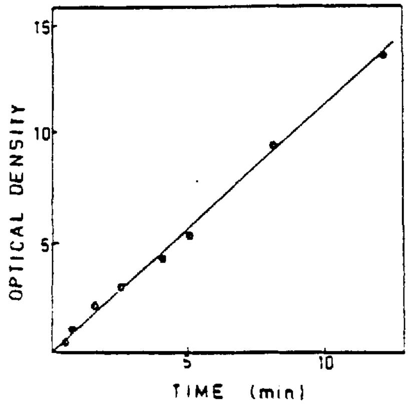


FIG. 10. Optical density at 510 mμ of the complex Fe^{2+}—1,10-phenanthroline vs the time of irradiation of a solution of potassium ferrioxalate at 0.006 mole/liter.

(1.11×10^4 liters/mole) and from Avogadro's number and the quantum yield of this photoreaction (1.25 at 253 Å), it becomes easy to determine the number of photons absorbed; $N_{abs,T} = 3.5 \times 10^{15}$ photons/5 ml/sec. The theoretical number of photons absorbed by the whole solution was given in the relations (4) and (6):

$$N_{abs,T} = \alpha \Sigma (N_L)_{\Delta\lambda} (T_F)_\lambda (T_Q)_\lambda (10^{D\lambda} - 1/10^{D\lambda}) \qquad (10)$$

$(N_L)_{\Delta\lambda}$ is given in Table 2; $(T_Q)_\lambda$ and $(T_F)_\lambda$ for the filter 2537 are given in Fig. 7. Moreover $(10^{D\lambda} - 1)/10^{D\lambda} = 1$ because the optical density of the actinometric solution at 0.006 mole/liter is never less than 6 in the wavelength range considered. Therefore, the product of the factors included in the Σ of relation (10) is easily evaluated: 4.19×10^{18} photons/5 ml/sec. The factor α is determined by the relation (10) knowing $N_{abs,T}$ and Σ:

$$\alpha = \frac{3.35 \times 10^{15} \text{ photons/sec 5 ml}}{4.19 \times 10^{18} \text{ photons/sec 5 ml}} \; 0.8 \times 10^{-3} \qquad (11)$$

Now, it becomes possible to calculate the number of photons absorbed by the complex and the noncomplexed species at each individual Hg line of

TABLE 3. Number of Photons Absorbed per Second by the Noncomplexed Different Filters and for (DVE) = (FN) = 0.6 mole/liter[a,b]

Filter λ (mμ)	954 A	954 B	930 A	930 B	930 + 954 A	930 + 954 B	053 A	053 B	053B A
366	0.72	13.2	0.70	12.7	0.65	11.7	0.70	12.7	0.61
334	0.76	15.2	0.73	14.5	0.65	13.0	0.73	14.5	0.51
313	1.73	141	1.5	123	1.33	108	1.4	115	0.73
302	0.76	76.5	0.66	59.5	0.60	53.5	0.54	48.4	0.22
297	0.56	43.1	0.42	32.5	0.36	28.0	0.28	21.5	0.1
289	0.31	16.0	0.22	11.3	0.18	9.55	0.08	4.32	0.02
280	0.5	19.5	0.32	12.6	0.27	10.6	0.04	1.66	0.01
275	0.22	6.52	0.12	3.98	0.11	3.25	0.01	0.17	
270	0.48	8.87	0.28	5.2	0.22	4.17	0.01	0.03	
265	3.0	33.2	1.67	18.6	1.33	14.7			
257	2.62	9.95	1.31	5.45	1.08	4.12			
254	14.5	32.4	7.85	17.2	6.02	13.2			
248	12.4	4.4	6.70	2.37	4.7	1.66			
240	11.2		6.25		3.64				
238	12.6		6.75		3.47				
236	11.0		5.85		2.82				
232	5.75		2.63		0.86				
222	3.05		1.14		0.16				

[a] A = $(N_{abs,NC})_{\Delta\lambda} \times 10^{-14}$.

[b] B = $(N_{abs,C})_{\Delta\lambda} \times 10^{-14}$.

wavelength at the different concentrations and for the different filters. The results are tabulated in Tables 3, 4, and 5. Moreover, the total number of photons absorbed by the whole solution, the complex, and the noncomplexed species are determined for the different filters and the

Species and by the Complex at Different Wavelength Ranges for the

	054		930 + 954 + 054		052		2537		2000
B	A	B	A	B	A	B	A	B	A
11.1	0.70	12.7	0.59	10.7	0.44	7.96			
10.1	0.68	13.7	0.56	11.1	0.01	0.03			
60	0.69	56.8	0.48	39.5					
20.4	0.02	2.21	0.01	1.27					
7.67									
1.18								0.03	
0.28							0.01	0.46	
0.01							0.01	0.40	
							0.05	1.02	
							0.52	5.81	
							0.67	2.54	
							4.2	9.30	
							4.2	1.48	
							2.36		
							1.96		
							0.80		
							0.26		
							0.03		0.66

different concentrations by addition of the values given in Tables, 3, 4, and 5. The final results as calculated are presented in Table 6.

Results of Photopolymerization and Discussion

The mean values of the rate of photopolymerization under different experimental conditions are detailed in Table 7. The number of experiments for each experimental condition and the standard deviation

TABLE 4. Number of Photons Absorbed per Second by the Noncomplexed Species and by the Complex at Different Wavelength Ranges for the Different Filters and for (DVE) = (FN) = 0.9 mole/liter[a,b]

Filter λ (mμ)	954		054		2537		2000	
	A	B	A	B	A	B	A	B
336	1.02	27.06	0.99	26.03				
334	0.66	21.28	0.59	19.18				
313	1.17	143.80	0.47	57.93				
302	0.48	77.26	0.01	2.23				
297	0.34	43.21						
289	0.20	16.11				0.03		
280	0.34	19.66			0.01	0.46		
275	0.14	6.60			0.01	0.40		
270	0.31	9.04			0.03	1.04		
265	2.01	34.19			0.34	5.99		
257	1.88	10.69			0.48	2.75		
254	10.73	36.17			3.10	10.40		
248	9.92	6.88			3.36	2.32		
240	11.20				2.36			
238	12.60				1.96			
236	11.00				0.80			
232	5.75				0.26			
222	3.05				0.03			0.66

[a] $A = (N_{abs,NC})_{\Delta\lambda} \times 10^{-14}$.

[b] $B = (N_{abs,C})_{\Delta\lambda} \times 10^{-14}$.

are presented in the same table. It is observed that the standard deviation in some cases takes relatively high values; however, not higher than 30%. It is well known that photoreactions are very sensitive to several factors. Fortunately, these errors do not affect the general trend of the results.

TABLE 5. Number of Photons Absorbed per Second by the Noncomplexed Species and by the Complex at Different Wavelength Ranges for the Different Filters and for (DVE) = (FN) = 1.2 moles/liter[a,b]

Filter λ (mμ)	954		054		2537		2000	
	A	B	A	B	A	B	A	B
336	1.23	45.27	1.20	43.56				
334	0.60	24.62	0.54	22.19				
313	0.88	193.17	0.35	77.81				
302	0.34	77.26	0.01	2.23				
297	0.26	43.40						
289	0.15	16.16				0.03		
280	0.22	19.78			0.01	0.46		
275	0.11	6.63			0.01	0.40		
270	0.24	9.11			0.02	1.05		
265	1.56	34.64			0.27	6.06		
257	1.44	11.13			0.37	2.84		
254	8.41	38.49			2.43	11.07		
248	10.36	6.44			3.73	1.95		
240	11.08				2.36			
238	12.60				1.96			
236	11.00				0.80			
232	5.75				0.26			
222	3.05				0.03			0.66

[a] $A = (N_{abs,NC})_{\Delta\lambda} \times 10^{-14}$.

[b] $B = (N_{abs,C})_{\Delta\lambda} \times 10^{-14}$.

The polymers obtained by AIBN initiation and photoinitiation possess the same characteristics. Their IR are identical with characteristic absorptions of cyano and ether groups at 2260 and 1100 cm^{-1}. Molecular

TABLE 6. Total Number of Photons Absorbed per Second by the Noncomplexed Species, by the Complex, and by the Whole Solution for the Different Filters and the Different Concentration Conditions

Filter	954	930	930 + 954	053	053B	054	930 + 954 + 054	052	2537	2000
(DVE) = (FN) = 0.6 mole/liter										
$N_{abs,NC} \times 10^{-14}$	81.16	45.10	28.45	3.79	2.20	2.09	1.64	0.45	15.07	0.66
$N_{abs,C} \times 10^{-14}$	419.84	318.84	275.45	218.28	110.74	85.41	62.57	7.99	21.04	-
$N_{abs,T} \times 10^{-14}$	501	363.94	303.9	222.07	112.94	87.50	64.21	8.44	36.11	0.66
$N_{abs,T}\Phi_T \times 10^{-14}$	6.52	3.74	2.69	0.672	0.339	0.262	0.192	0.025	1.07	0.099
(DVE) = (FN) = 0.9 mole/liter										
$N_{abs,NC} \times 10^{-14}$	72.80					2.06			12.74	0.66
$N_{abs,C} \times 10^{-14}$	451.95					105.37			23.37	-
$N_{abs,T} \times 10^{-14}$	524.75					107.43			36.11	0.66
(DVE) = (FN) = 1.2 moles/liter										
$N_{abs,NC} \times 10^{-14}$	69.18					2.10			12.25	0.66
$N_{abs,C} \times 10^{-14}$	526.10					145.79			23.86	-
$N_{abs,T} \times 10^{-14}$	595.38					147.89			36.11	0.66

TABLE 7. Rates of Photopolymerization and Standard Deviations of the Rate (σ), Molar Fractions of FN in the Copolymer (m_{FN}) and Molecular Weights (MW), Number of Polymeric Molecules Formed per Second (N_{pm}) and Mean Quantum Yield of the Filters, for Different Filters and Different Concentration Conditions

Filter	(DVE) + (FN) (moles/liter)	Rate (mg/5 mls, sec × 10^4)	σ (mg/5 ml, (sec × 10^4)	m_{FN}	MW	N_{pm}/sec (5 ml × 10^{-14})	Φ_T[c]	Number of experiments in each condition
954	1.2	23.83	7.06	0.667	4000	3.58	0.007	6
954	1.8	57.62	0.42	0.673	(5200)[a]	(7.10)	(0.0135)	2
954	2.4	91.75	5.75	0.673	-	-	-	3
930	1.2	17.97	6.10	0.637	4600	2.37	0.0065	4
930+ 954	1.2	17.07	7.01	0.684	3900	2.64	0.0087	4
053	1.2	4.37	0.12	-	-	-	-	2
053B	1.2	3.38	0	-	-	-	-	1
054	1.2	2.81	0.78	0.625	4700	0.36	0.0041	9
054	1.8	6.87	2.46	0.657	(5200)[a]	(0.794)	(0.0074)	3
054	2.4	15.47	6.25	0.638	-	-	-	3
930+ 954+ 054	1.2	2.98	1.05	0.660	-	-	-	4
052	1.2	≃0	-	-	-	-	-	1
2537	1.2	8.88	2.14	0.637	4600	1.16	0.032	3
2537	1.8	17.70	3.46	0.665	(5500)[a]	(1.93)	(0.053)	3
2537	2.4	23.92	2.82	0.623	-	-	-	3
2000	1.2	0.92	0.21	0.530	-[b]	-	-	2
2000	1.8	1.87	0.26	0.584	-[b]	-	-	2
2000	2.4	2.69	0.46	0.592	-[b]	-	-	2

---

[a] These polymers were not completely dissolved. The molecular weights are probably slightly higher than the indicated values.

[b] Solubility of these polymers is very poor.

[c] Directly calculated from N_{pm} and $N_{abs,T}$.

weights are of the same order of magnitude; moreover, the molar fraction of FN in the copolymer is approximately constant (0.60 - 0.67), indicating an alternating structure of 1:2 composition. However, the molar fraction of FN in the copolymers obtained by irradiation with the filter 2000 was lower. With this filter the light is essentially absorbed by the noncomplexed species, therefore the initiation must be due to excited state monomers. Moreover, these polymers are not very soluble. These facts indicate that during polymerization some double bonds are occasionally able to cross-link, leading to the insoluble character and a composition between 1:1 and 1:2. The reason for such phenomena is not well explained; it could be due to the initiation itself or to some kind to propagation via light-excited species.

It was shown earlier that the copolymerization initiated by AIBN indicated an order 1.5 and an order 1 for the total monomer concentration and the AIBN concentration, respectively. As described further, the rate of photopolymerization follows the same law, indicating that both kinds of initiation lead to similar polymerization mechanisms.

Figure 11 shows that the rate of photopolymerization is approximately a function of the 1.2 power of the number of photons absorbed by the whole solution (only, however, for the filters 930, 954, 054, and their combinations!), the 1.2 power of the number of photons absorbed by the complex (only also for the filters 930, 954, 054, and their

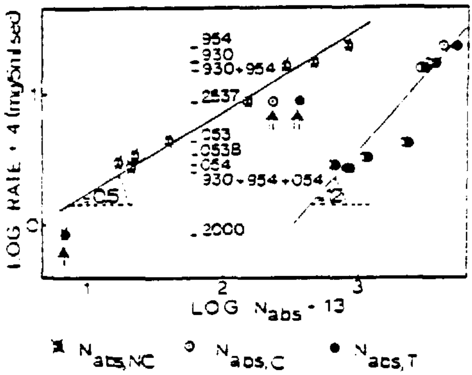


FIG. 11. Dependence of the number of photons absorbed by the noncomplexed species, the complex, and the whole solution on the rate of photopolymerization in methanol at 26-28°C. (DVE) = (FN) = 0.6 mole/liter. The numbers indicate the catalog numbers of the filters. Similar curves can be obtained for other concentrations.

combinations), and the half power of the number of photons absorbed by the noncomplexed species. At first sight it appears that the polymerization is preferentially initiated by the noncomplexed species since all the points plotted for the number of photons absorbed by the complex or the whole solution present two exceptions with anomalous high rates (see arrows in Fig. 11 for the filters 2000 and 2537). However, the present statement is probably not valid as shown below. It is important to note that the dependence of the number of photons absorbed on the rate of polymerization is apparent and has absolutely no significance without consideration of the molecular weights of the polymers and the quantum yields of polymerization at each individual wavelength.

Even if the rates observed with the different filters attest important differences (the rate with the filter 954 is 9 times higher than with the filter 054), the molecular weights present constant values, at least when the concentration is constant. From the traditional relations [9] over the rate of polymerization, one concludes that the rate of polymerization initiated by UV, as well as the AIBN-initiated polymerization, must follow a first-order dependence of the number of "effective" species formed per time unit, an "effective" specie being a specie which can effectively initiate the polymerization. Let E represent this number:

$$\text{rate} = kE \tag{12}$$

The number E depends on the number of photons absorbed multiplied by the quantum yield Φ:

$$E = \Phi N_{abs} \tag{13}$$

It can be shown that the polymerization cannot be initiated <u>only</u> by the noncomplexed species, at least when the photons are absorbed by the complex and noncomplexed species together (that is, the case for all the filters except the filter 2000 as described in Table 6). Thus if the polymerization were initiated only by the noncomplexed species, one would obtain, on the basis that the rate must follow a first-order dependence of the number of "effective" species:

$$\text{rate} = kE_{NC} \tag{14}$$

E_{NC} is the number of "effective" species formed per second relative to the noncomplexed species. Moreover,

$$E_{NC} = \Sigma(D_{NC})_{\Delta\lambda} \tag{15}$$

where $(E_{NC})_{\Delta\lambda}$ is the fraction of E_{NC} in a wavelength range $\Delta\lambda$. As stated in relation (13), one obtains:

$$(E_{NC})_{\Delta\lambda} = (\Phi_{NC})_{\lambda}(N_{abs,NC})_{\Delta\lambda} \tag{16}$$

$(\Phi_{NC})_{\lambda}$ being the quantum yield of the polymerization at wavelength $(\lambda_2 + \lambda_1)/2$ relative to the noncomplexed species. Combining the relations (14), (15), and (16):

$$\begin{aligned}\text{Rate} &= k\Sigma(\Phi_{NC})_{\lambda}(N_{abs,NC})_{\Delta\lambda}\\ &= k\,\Phi_{NC}\Sigma(N_{abs,NC})\\ &= k\,\Phi_{NC}N_{abs,NC}\end{aligned} \tag{17}$$

where Φ_{NC} is a mean factor of the quantum yield for a <u>given</u> filter relative to the non-complexed species. It is important to note that $(\Phi_{NC})_{\lambda}$ is independent of the filter used and depends only on the wavelength, while Φ_{NC} is a mean factor for the different wavelengths which therefore cannot be correlated by mathematical relations to $(\Phi_{NC})\lambda$ except for filters transmitting monochromatic light!

The fact that the rate shows an apparent half-power dependence of the number of photons absorbed by the noncomplexed species was previously stated:

$$\text{rate} = k'\,(N_{abs,NC})^{1/2} \tag{18}$$

For an agreement between relations (17) and (18), one would obtain:

$$\Phi_{NC} = \text{function of } (N_{abs,NC})^{-1/2} \tag{19}$$

Such an expression means that Φ_{NC} must increase when $N_{abs,NC}$ decreases, and inversely.

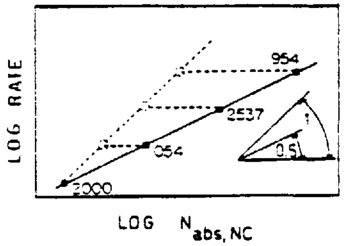


FIG. 12. Simplified representation of the log of the rate vs the log of $N_{abs,NC}$ for the filters 954, 2537, 054, and 2000.

Figure 12 shows a simplified representation of the observed rates vs $N_{abs,NC}$ where one observes that the following sequence for the filters 2000, 2537, 054, and 954 must be found for passing from a slope 0.5 to a slope 1:

$$(\Phi_{NC})_{2000} > (\Phi_{NC})_{054} > (\Phi_{NC})_{2537} > (\Phi_{NC})_{954} \tag{20}$$

(As shown in Fig. 12, the absolute values of Φ_{NC} show a reverse sequence! In fact, however, the quantum yield is smaller than unity, as shown below, so that negative log values must be considered). The sequence (20) is, however, practically impossible to establish as shown in the simplified representation of the transmittance of these filters (Fig. 13). Indeed, if the quantum yield decreases when the wavelength increases (that can be generally expected), the analysis of Fig. 13 leads to the conclusion:

$$(\Phi_{NC})_{2000} > (\Phi_{NC})_{2537} > (\Phi_{NC})_{954} > (\Phi_{NC})_{054} \tag{21}$$

Even if the quantum yield increases when the wavelength increases (less probable), the reverse sequence will be found, so that no sequence as required in relation (21) can be established except that if irregular variations of the quantum yield with the wavelength is assumed. Such a possibility is highly improbable.

One concludes that the initiation cannot be due only to the noncomplexed species when the photons are absorbed by the complex and the noncomplexed species together. But, since the polymerization occurs with the filter 2000 for which only the noncomplexed species

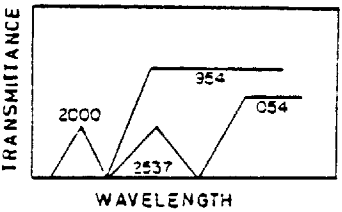


FIG. 13. Simplified representation of the transmittance of the filters 954, 2537, 054, and 2000.

absorb the incident photons, one must admit that the noncomplexed species may initiate the polymerization. Therefore, the final conclusion is that the polymerization can be initiated both by the complex and the noncomplexed species when both the complex and the noncomplexed species absorb the incident photons; it seems reasonable to suppose that their relative contributions in the initiation step correspond to some extent to their relative absorption. The present conclusion may not be too surprising; the above developments bring only supplementary support for this conclusion through some physicomathematical considerations. The rate is thus expressed by

$$\text{rate} = kE_T \qquad (22)$$

where E_T is the total number of "effective" species in the whole solution. In the same manner as described above, one obtains

$$\text{rate} = k\Phi_T N_{abs,T} \qquad (23)$$

where Φ_T is the mean quantum yield for a <u>given</u> filter relative to all the excited species in the solution. It was already observed that for the filters 954, 930, 054, and their combinations

$$\text{rate} = k(N_{abs,T})^{1.2} \qquad (24)$$

A correlation between the relations (23) and (24) gives

$$\Phi_T = \text{function of } (N_{abs,T})^{0.2} \qquad (25)$$

The quantum yield increases with the number of photons absorbed by the whole solution. This relation is only valid, however, for the filters 954, 054, 930, and their combinations.

Moreover, the rates with the filters 2537 and 2000 were abnormally high (see arrows in Fig. 11). In order to obtain a first-order dependence of the total number of "effective" species for any filter, the mean quantum yield of the filter must follow the sequence (as shown in the simplified representation, Fig. 14):

$$(\Phi_T)_{2000} > (\Phi_T)_{2537} > (\Phi_T)_{954} > (\Phi_T)_{054} \qquad (26)$$

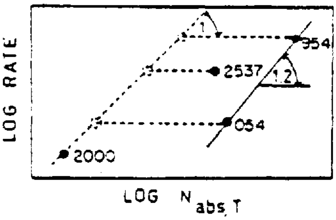


FIG. 14. Simplified representation of the log of the rate vs the log of $N_{abs,T}$ for the filters 954, 2537, 054, and 2000.

It is remarkable that this sequence is in full accord with the concept of an increase of the quantum yield with a decrease of the wavelength as already stated in relation (21).

Filters 2000, 2537, and 054 are especially interesting because they cover a small range of the spectrum. From Fig. 14 (or 11) it is possible to determine the relative values of the quantum yield for these filters:

$$(\Phi_T)_{2000} = 5(\Phi_T)_{2537} = 50(\Phi_T)_{054} \qquad (27)$$

From the molecular weights and the rate measurements it is quite possible to calculate the number of polymeric molecules N_{pm} formed per second (Table 7). Dividing this number by the number of photons absorbed, the quantum yield for a given filter is obtained (Table 7). At (DVE) = (FN) = 0.6 mole/liter, it is found that

$$(\Phi_T)_{2537} \simeq 0.03$$

$$(\Phi_T)_{0.54} \simeq 0.003$$

and from the relation (27)

$$(\Phi_T)_{2000} \simeq 0.15 \tag{28}$$

As indicated above, these filters cover small ranges of the spectrum and their quantum yields can be approximately equated to the quantum yields of these wavelength ranges:

$$\begin{aligned} (\Phi_T)_{\lambda < 225\text{m}\mu} &= 0.15 \\ (\Phi_T)_{225\text{m}\mu < \lambda < 280\text{m}\mu} &= 0.03 \\ (\Phi_T)_{\lambda < 280\text{m}\mu} &= 0.003 \end{aligned} \tag{29}$$

The interest of these approximations lies in the fact that it becomes possible to determine $N_{abs,T}\,\Phi_T$ for the filters covering larger wavelength ranges. Indeed, from the relation

$$N_{abs,T}\,\Phi_T = \Sigma(N_{abs,T})_{\Delta\lambda}(\Phi_T)_\lambda \tag{30}$$

$N_{abs,T}\,\Phi_T$ can be evaluated taking the values of $(N_{abs,T})_{\Delta\lambda}$ already given in Table 3 and the values of $(\Phi_T)_\lambda$ given in relation (29). The values of $N_{abs,T}\,\Phi_T$ are tabulated in Table 6 while the plot of the log of the rate vs the log of $N_{abs,T}\,\Phi_T$ is given in Fig. 15. It is absolutely remarkable that all the points are approximately on a line of slope 1, indicating a first-order dependence of the number of effective species initiating the polymerization. The points for the filters 2000, 2537, and 054 are evidently on a line of slope 1 since one started from the values of their quantum yield for all the calculations and approximations. However, the fact that the points for the filters 930, 954, and their combinations are on the same line indicates at least that the method of calculation is adequate and that the conclusion concerning an initiation by the excited state of all the species (complex and noncomplexed) appears correct. Similar considerations might be drawn for the other concentrations in DVE and FN. Relation (27) is still valid; however, absolute values of the quantum yield as indicated in the relations (28) cannot be determined since the molecular weight measurements are not sufficiently precise due to the partial insolubility of the polymers. Nevertheless, the relative values given in relation (27) might be considered, and the log of the rate vs the log of $N_{abs,T}\,\Phi_T$ would also lead to a line of slope 1 (the difference would lie in the fact that $N_{abs,T}\,\Phi_T$

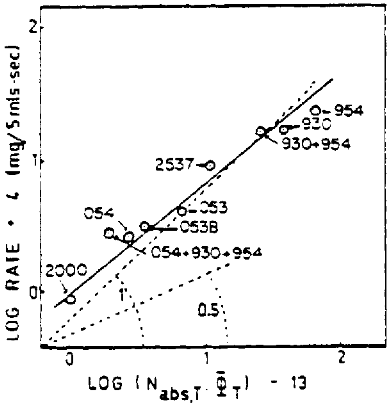


FIG. 15. Dependence of the total number of photons absorbed by the whole solution multiplied by the quantum yield (as indicated in Eq. 30) on the rate of photopolymerization. (DVE) = (FN) = 0.6 mole/liter. The numbers refer to the catalog numbers of the filters.

would be given with the approximation of a constant). Absolute values as given in the relations (28) might also be taken for the other concentrations; however, there is no proof that the values of the quantum yield remain constant with the monomer concentration. This important question, which was not completely resolved in our experiments, is, however, discussed briefly in the last part of this paper.

The last experiments were concerned with the dependence of the total monomer concentration on the rate of polymerization using four typical filters (954, 054, 2537, and 2000). The log of the rate vs the log of the total monomer concentration is given in Fig. 16, and one observes that the order is 2.5, 1.9, 1.5, and 1.5, respectively, for the filters 054, 954, 2537, and 2000. An order 1.5 was expected since this order was found for the AIBN-initiated polymerization. The orders 2.5 and 1.9 are apparent orders. Indeed, with the filters 054 and 954 an increase of the concentration increases the optical density at the same time, and therefore the number of photons absorbed, and also the number of effective species initiating the polymerization; while with the filters 2000 and 2537 the optical density is already so high that in all cases all the photons are absorbed, so that $N_{abs,T}$ remains constant (see Table 6). The rate is therefore expressed by

$$\text{rate} = [(\text{DEV}) + (\text{FN})]^n (N_{abs,T}\, \Phi_T) \qquad (31)$$

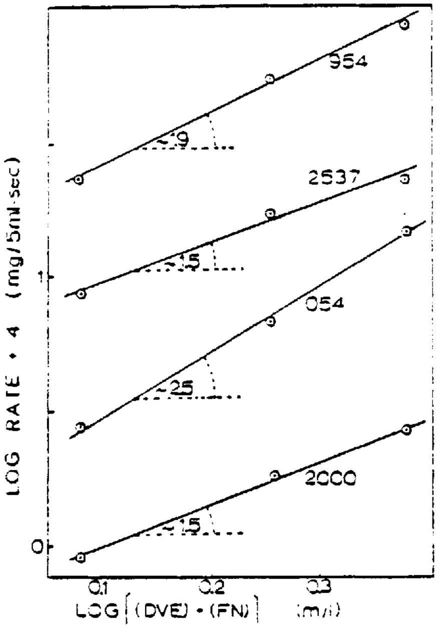


FIG. 16. Dependence of the total monomer concentration on the rate of photopolymerization for four different filters. (DVE) = (FN).

The supposition may be made that Φ_T remains constant for a given filter. Since $N_{abs,T}$ is a function of the monomer concentration (at least under the present concentration conditions for the filters 954 and 054), the order n is found by the plot of the log of the rate divided by $N_{abs,T}$ vs the log of total monomer concentration (Fig. 17). In all cases n = 1.5. It is evident for the filters 2000 and 2537 because for these filters $N_{abs,T}$ is constant, but for the other two filters the passage from an order higher than 1.5 to an order 1.5 represents a result of highest interest indicating once again that the method of calculation of the number of photons absorbed is correct and precise.

It is shown in another paper [7] that in the DVE-maleic anhydride copolymerization initiated by AIBN, the efficiency of the initiator always increases with an increase of the monomer concentration. The efficiency was evaluated by the nitrogen analysis of the polymer since the nitrogen presence is only due to the decomposition of the

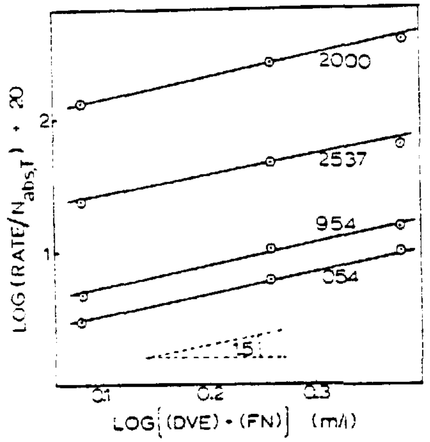


FIG. 17. Dependence of the total monomer concentration on the rate of photopolymerization divided by the total number of photons absorbed in the case of four different filters (DVE) = (FN).

initiator. The order of monomer concentration varies between 1 and 2; but by calculations, including the efficiency of the initiator and the order of the AIBN concentration, it is shown that the true order of the monomer concentration is close to 1 and is generally expected for the polymerization.

It is therefore reasonable to assume that the order 1.5 observed in the DVE-FN polymerization initiated by AIBN is also an apparent order. Unfortunately, we were not able to make the same approximations as we did for the DVE-maleic anhydride system, since in the DVE-FN system the percentage of nitrogen due to the decomposition of AIBN cannot be determined because there is a high nitrogen content due to the fumaronitrile.

Similarly, it can be assumed that the order 1.5 of the photopolymerization is apparent and due to the change of the efficiency, i.e., the quantum yield, with the monomer concentration. Unfortunately, here also no precise results can be obtained since the quantum yields were not determined for concentrations other than 0.6 mole/liter. Nevertheless, if it is presumed that the true order is 1, one must necessarily conclude that the quantum yield is a function of the half power of the monomer concentration.

APPENDIX

The intensity of the light absorbed I_{abs} is related to the incident intensity I_0 by

$$I_{abs} = I_0 \frac{10^D - 1}{10^D}$$

where D is the optical density of the solution, and

$$D = \epsilon cd$$

where ϵ is extinction coefficient, c is the concentration, and d is the thickness of the cell. When the concentration is constant, D = ad where a is a constant (= ϵ c). In the present paper, a = $(\epsilon_\lambda c)_{NC}$ + $(\epsilon_\lambda c)_C$ (see relation 9).

The value of $(10^D - 1)/10^D$ is easily determined for a square cell because the thickness is constant. However, when the solution is in a tube, the problem becomes more complicated since d takes different values. A mean value of $(10^D - 1)/10^D$ must be calculated. The term $(10^D - 1)10^D$ may be represented by the symbol Z.

The solution in the tube can be divided in two parts: the bottom of spherical shape and a cylindrical part above. In a cartesian coordinate system, as indicated in Fig. 18 the coordinate d is related to the coordinates x and y as follows: 1) In the cylindrical part

$$d = 2(r^2 - x^2)^{1/2}$$

where r is the radius of the tube, and

$$Z = \frac{10^{2a}(r^2 - x^2)^{1/2} - 1}{10^{2a}(r^2 - x^2)^{1/2}} = Z_c$$

2) In the spherical part

$$d = 2(r^2 - x^2 - y^2)^{1/2}$$

and

$$Z = \frac{10^{2a}(r^2 - x^2 - y^2)^{1/2} - 1}{10^{2a}(r^2 - x^2 - y^2)^{1/2}} = Z_s$$

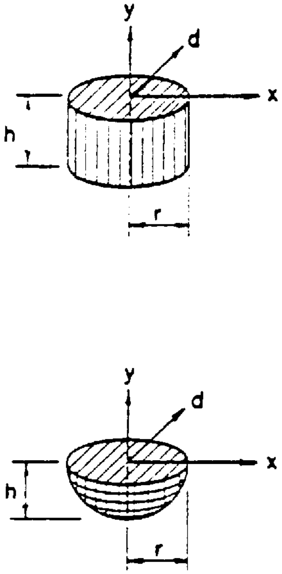


FIGURE 18.

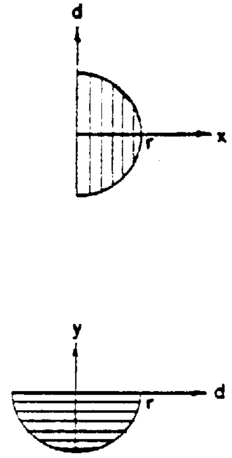


FIGURE 19.

Z_c and Z_s are the typical values of Z for the cylindrical and spherical parts.

For continuous variation of x and y, the integrals of Z_c and Z_s do not afford direct solutions so that the use of a computer is necessary to solve the problem by approximation. The problem is symetrical versus the x axis: thus one may consider only one half of the tube as represented by the top and side view of the tube (see Fig. 19).

x is divided between x = 0 and x = r in m parts, and the value of x in the middle of each division is

$$x = \frac{2n+1}{2m} r \qquad n = 0, 1, 2, \ldots, m-2, m-1$$

y is divided between y = 0 and y = r in p parts, and the value of y in the middle of each division is

$$y = \frac{2q+1}{2p} r \qquad q = 0, 1, 2, \ldots, p-2, p-1$$

One obtains: 1) For the cylindrical part

$$d = 2\left[r^2 - \left(\frac{2n+1}{2m} r\right)^2\right]^{1/2}$$

2) For the spherical part

$$d = 2\left[r^2 - \left(\frac{2n+1}{2m} r\right)^2 - \left(\frac{2p+1}{2p} r\right)^2\right]^{1/2}$$

That m = p may be assumed in order to simplify the problem. The values of Z_c and Z_s are sums of the values at each individual division divided by the number of divisions. After some adequate transformations, one obtains

$$Z_c = \frac{\displaystyle\sum_{n=0}^{n=m-1} \frac{10^{a(r/m)[4m^2 - (2n+1)^2]^{1/2}} - 1}{10^{a(r/m)[4m^2 - (2n+1)^2]^{1/2}}}}{m}$$

$$Z_s = \frac{\displaystyle\sum_{q=0}^{q=m-1}\sum_{n=0}^{n=m-1} \frac{10^{a(r/m)[4m^2-(2n+1)^2-(2q+1)^2]^{1/2}} - 1}{10^{a(r/m)[4m^2-(2n+1)^2-(2q+1)^2]^{1/2}}}}{m^2-\gamma}$$

Note: For Z_s the number of divisions is less than m^2 (see Fig. 20) since for some values of n and q the factor $4m^2 - (2n + 1)^2$ is less than 0. So the $\Sigma\Sigma$ must be divided by a number less than m^2, in this case $m^2 - \gamma$. The term γ was also evaluated by computer.

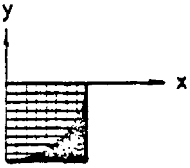


FIGURE 20.

In the present paper the values of Z_c and Z_s were determined taking $m = 50$ (in that case, $\gamma = 535$) for different values of ar chosen arbitrarily, or different values of a since r is fixed at 1.1 cm.

However, the problem is not completely solved because a mean value of Z is needed for the two parts of the tube. Z depends on Z_c, Z_s, and the relative cross sections of the cylindrical and spherical parts. The cross section of the cylindrical part is 2rh and for the spherical part is $\pi r^2/2$. So

$$Z = \frac{Z_c 2rh + Z_s \pi r^2/2}{2rh + \pi r^2/2}$$

The tube is filled with 5 ml and the radius is 1.1 cm. Therefore, $2rh = 1.28\ \text{cm}^2$ and $\pi r^2/2 = 1.9\ \text{cm}^2$.

A plot of Z vs arbitrary values of a is given in Fig. 21. This plot permits the determination of Z for any value of a. The values of Z corresponding to the values of a in the present paper were plotted vs the wavelengths in Fig. 8.

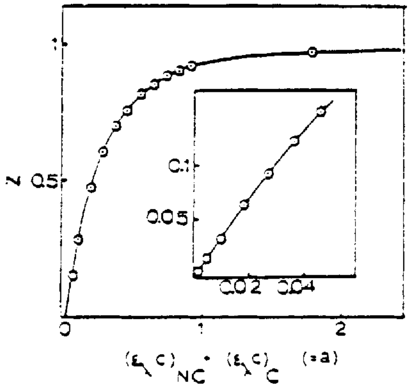


FIG. 21. Values of $(10^{ad} - 1)/10^{ad}$ vs arbitrary values of "a" for continuous variations of d from 0 to 2.2.

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