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BENZIL/*N*,*N*-DIMETHYLAMINOETHYL METHACRYLATE SYSTEM AS PHOTOINITIATOR FOR METHYL METHACRYLATE POLYMERIZATION

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ABSTRACT

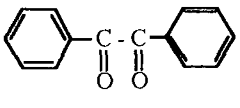
Photopolymerization of MMA in bulk and an air atmosphere at 20°C was studied using the benzil/*N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) combination as photoinitiator. The polymerization rate (R_p) was proportional to the 0.3 power of the benzil concentration and the 0.6 power of the DMAEMA concentration. R_p reaches a maximum and then declines as either the benzil concentration is increased (>0.03 M) or the DMAEMA concentration is increased (>0.01 M). The termination of polymerizatin was found to be bimolecular. DMAEMA can also act as a chain transfer agent; its chain transfer constant was evaluated to be 0.093. The methacrylate moiety of DMAEMA can participate in the polymerization process and cause crosslinking.

INTRODUCTION

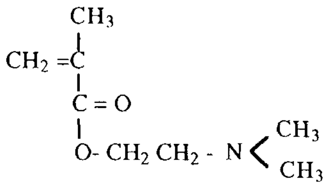
Aromatic carbonyl compounds form the most important class of commercial photoinitiators, widely used in combination with tertiary amines for the photopolymerization or curing of vinyl monomers or prepolymers [1, 2]. The amine acts as an oxygen scavenger and also as a co-synergist with aromatic ketone in accelerating the polymerizatin process. However, the use of simple aromatic or aliphatic amines gives rise to some problems associated with migration or the incompatibility of the amine. Amines also act as chain transfer agents by a standard hydrogen abstraction mechanism, decreasing the molecular weight of the prepared polymer. One way to minimize the above problems is to incorporate the amine functional groups into monomers which themselves are capable of participation in the polymerization process [3]. Thus, it was demonstrated that *N,N*-dialkylaminoethyl methacrylates are quite effective in accelerating the photopolymerization of air-saturated 1,6-hexanediol diacrylate induced by benzoin isopropyl ether [4].

The photopolymerization of methyl methacrylate induced by a combination comprising a carbonyl compound and an amine has been studied by several investigators. In particular, the benzil/amine system has been examined [5-9], because it is widely used as a good photoinitiator [10], but opinions differ as to exact mode of photoinitiation.

In this paper we report the results of kinetic studies of the photopolymerization of methyl methacrylate using the benzil/*N,N*-dimethylaminoethyl methacrylate (DMAEMA) combination as a photoinitiator.



(Benzil)



(DMAEMA)

EXPERIMENTAL

Methyl methacrylate (MMA), *N,N*-dimethylaminoethyl methacrylate (DMAEMA), and triethylamine (TEA) were from Merck and used after vacuum distillation. Benzil (98%) was from Aldrich and used without further purification.

Polymerizations were carried out in Pyrex tubes. The required amounts of MMA and photoinitiator (benzil and DMAEMA) were charged into tubes which were stoppered and placed in a bath thermostated at 20°C. The samples were irradiated under air atmosphere by a Hanovia 450-W high pressure arc lamp. Surrounding the lamp was a window-glass filter (thickness 2 mm, $\lambda > 310$ nm) and a quartz well through which cooling water was pumped. Tubes were placed 10 cm from the lamp. The polymers that formed at low concentrations after a given time were removed from the tube and isolated by precipitation in acidified cold methanol followed by drying at 70°C under vacuum to constant weight.

The intrinsic viscosities $[\eta]$ of the polymers were determined by measurements in benzene solution at 30 ± 1°C by an Ubbelohde viscometer. The number-average molecular weights ($\overline{M}_n$) of the polymers were then calculated from viscosity data by using the equation [11]:

$$[\eta] = 8.69 \times 10^{-5}\overline{M}_n^{0.76}$$

RESULTS AND DISCUSSION

Preliminary experiments on the bulk photopolymerization of MMA under air atmosphere at 20°C showed that the benzil/DMAEMA combination is an efficient photoinitiator for this system (Table 1). Rates of polymerization (R_p) were ob-

TABLE 1. Bulk Photopolymerization of MMA[a] at 20°C Induced by Various Photoinitiators

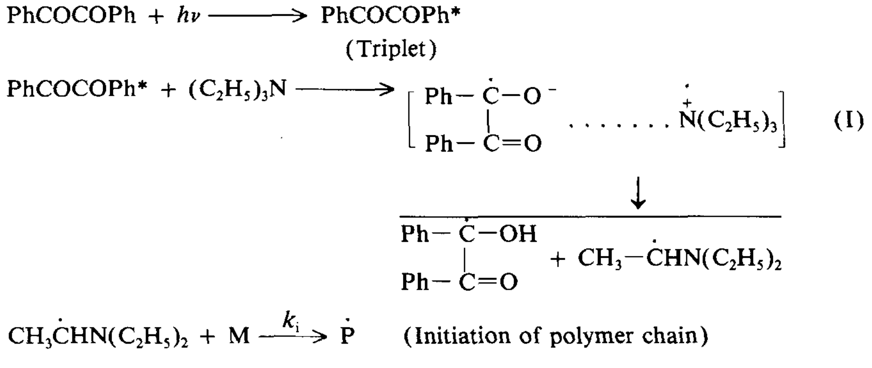
Photoinitiator	Concentration, mol/L	$R_p \times 10^4$ mol/L·s	$\overline{M}_n$
Benzil	0.1	0.56	131,700
Benzil/TEA	0.1/0.0119	1.05	28,300
Benzil/DMAEMA	0.1/0.0119	3.24	25,500
Benzil/DMAEMA	0.1/0.119	3.01	10,200
Benzil/DMAEMA	0.1/1.000	2.26	[b]

[a] [MMA] = 9.42 mol/L.

[b] Not determined because the polymer was insoluble in benzene (c = 0.2%, 30°C).

tained from the slopes of linear plots of percent conversion versus time (not shown). While no polymerization of MMA was observed in the absence of an initiator, polymerization with a small R_p took place in the presence of benzil after an inhibition time of 19 minutes. When TEA or DMAEMA was added with benzil, no inhibition period was observed and the R_p was much higher, especially in the case of DMAEMA. The $\overline{M}_n$ of the prepared polymers, obtained from viscosity measurements (in benzene, c = 0.5%) showed that the use of an amine caused a significant reduction in $\overline{M}_n$ (Table 1). However, when higher concentrations of DMAEMA were used, the prepared polymer was insoluble in benzene. Apparently DMAEMA incorporated into the polymer and caused crosslinking.

The photochemistry of the benzil-amine-vinyl monomer system has been extensively studied [5-9], and it seems to be different under different conditions of irradiation. Under conditions of lamp irradiation with long-wavelength light ($\lambda >$ 330 nm), the sequence of reactions in Scheme 1 is suggested to take place, which is in accordance with the general scheme of reactions proposed for ketone-amine systems.



$$\mathrm{PhCOCOPh} + h\nu \longrightarrow \underset{\text{(Triplet)}}{\mathrm{PhCOCOPh^*}}$$

$$\mathrm{PhCOCOPh^*} + (\mathrm{C_2H_5})_3\mathrm{N} \longrightarrow \left[\begin{matrix}\mathrm{Ph{-}\dot{C}{-}O^-} \\ | \\ \mathrm{Ph{-}C{=}O}\end{matrix} \;\cdots\cdots\; \dot{\overset{+}{\mathrm{N}}}(\mathrm{C_2H_5})_3\right] \quad \text{(I)}$$

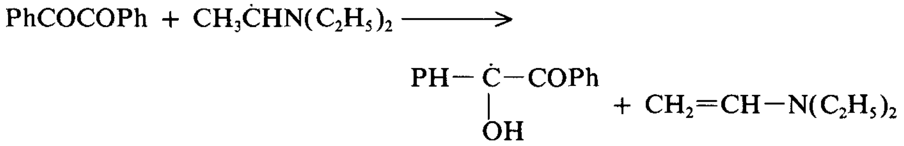
$$\downarrow$$

$$\begin{matrix}\mathrm{Ph{-}\dot{C}{-}OH} \\ | \\ \mathrm{Ph{-}C{=}O}\end{matrix} + \mathrm{CH_3{-}\dot{C}HN(C_2H_5)_2}$$

$$\mathrm{CH_3\dot{C}HN(C_2H_5)_2} + \mathrm{M} \xrightarrow{k_i} \dot{\mathrm{P}} \quad \text{(Initiation of polymer chain)}$$

SCHEME 1.

The decomposition of the charge transfer complex can lead to *free radicals*, as shown in Scheme 1, and/or to *ion radicals*, depending on the acid-base conditions of the system. In general, the formation of free radicals is favored in nonpolar solvents, while ion radical formation is favored in polar media. Encinas et al. [8] found that in the system MMA:benzene (1:1), the formation of free radicals is almost quantitative (100%), while in the more polar system MMA:acetonitrile (1:1), the yield of free radicals drops to 20%. The higher the yield of free radicals, the higher the efficiency of the complex as an initiator (I). The initiation of polymerization must be induced by the α-amine radicals because the reactivity of ketyl radicals toward the monomeric double bond is very low due to their high tendency to enter into radical coupling reactions (e.g., pinacolization) [12]. When the concentration of benzil is high, the α-amine radicals can also react with benzil to produce the corresponding ketyl radicals, causing a decrease in the efficiency of the initiator because the α-hydroxy radicals produced are unable to initiate the polymerization chain [13]:



$$\mathrm{PhCOCOPh} + \mathrm{CH_3\dot{C}HN(C_2H_5)_2} \longrightarrow \mathrm{PH{-}\underset{\displaystyle |\atop \displaystyle OH}{\dot{C}}{-}COPh} + \mathrm{CH_2{=}CH{-}N(C_2H_5)_2}$$

Sengupta et al. studied the kinetic behavior of the bulk photopolymerization ($\lambda > 280$ nm) of MMA induced by benzil/*N,N*-dimethylaniline [6] or benzil/TEA [7], and they suggested that the decomposition of the charge transfer complex of triplet benzil and amine yields diradicals rather than monoradicals, which means that both carbonyl groups of benzil are excited during irradiation. They also suggested that the pinacol radicals formed are responsible for primary radical termination, while the amine cation radicals present in the complex are effective in degradative initiator transfer [6, 7].

The photobehavior of benzil-amine-vinyl monomer system under irradiation with short wavelength light is quite different. Allen et al. [9], who studied this system under irradiation with 254 nm light and polychromatic light from a fluorescent lamp, reported that benzil primarily undergoes symmetric Norrish type I cleavage to produce benzoyl radicals which then abstract a hydrogen atom from the amine (Scheme 2).

$$\mathrm{PhCOCOPh} + h\nu \longrightarrow \mathrm{2Ph{-}\dot{C}O}$$

$$\mathrm{Ph{-}\dot{C}O} + \mathrm{(C_2H_5)_3N} \longrightarrow \mathrm{Ph{-}CHO} + \mathrm{CH_3\dot{C}HN(C_2H_5)_2}$$

SCHEME 2.

McGimpsey and Scaiano [14] reported that *laser* excitation of benzil leads to α-cleavage, which is not observed with lamp irradiation.

In the present work, in order to gain insight into the photopolymerization mechanism of MMA induced by the benzil/DMAEMA system irradiated with long wavelength light ($\lambda > 310$ nm) from a Hanovia high-pressure mercury lamp (450 W), the kinetic behavior of this polymerization was studied. The results obtained are presented in Table 2. It is observed that up to a certain concentration of DMAEMA (about 0.0119 M), the rate of polymerization increases to a maximum value which depends on the concentrations of both DMAEMA and benzil, and thereafter the rate decreases to a minimum value at which it remains practically constant (Fig. 1). Similar observations were made when the concentration of benzil was varied and the concentration of DMAEMA was kept constant (Fig. 2).

The plot of log R_p vs log[DMAEMA] given in Fig. 3 shows an initiator exponent value of 0.57 or 0.61, while the plot of log R_p vs [benzil] given in Fig. 4 shows an initiator exponent value of 0.29.

TABLE 2. Results of the Bulk Photopolymerization of MMA at 20°C with the Benzil/DMAEMA System as Photoinitiator[a]

$[B] \times 10^4$ mol/L	$[D] \times 10^4$ mol/L	$[B][D]^2 \times 10^6$ mol^3/L^3	$R_p \times 10^4$ mol/L·s	$[\eta]$, dL/g	$\overline{M}_n$	$\frac{10^3}{P_n}$
10	63	0.04	1.17	0.41	66,037	1.47
10	75	0.06	1.29	0.39	63,874	1.57
10	89	0.08	1.44	0.38	61,728	1.62
10	100	0.10	1.50	0.37	59,599	1.68
10	119	0.14	1.69	0.34	53,324	1.88
10	200	0.40	1.50	0.35	55,397	1.81
10	297	0.88	1.35	0.34	53,324	1.88
10	432	1.87	1.33	0.33	51,270	1.95
10	500	2.50	1.31	0.32	49,235	2.03
1000	29	0.84	1.35			
1000	59	3.48	1.90			
1000	89	7.92	2.59			
1000	119	14.16	3.24			
1000	297	88.21	3.06			
1000	432	186.62	2.99			
1000	590	348.10	2.97			
1000	863	744.77	2.92			
10	119	0.14	1.69	0.34	53,324	1.88
50	119	0.71	2.66	0.30	45,227	2.21
100	119	1.42	3.57	0.24	33,720	2.97
300	119	4.25	4.42	0.23	31,883	3.14
500	119	7.08	3.55	0.21	28,286	3.54
700	119	9.91	3.22	0.20	26,528	3.77
1000	119	14.16	3.24	0.19	24,796	4.04

[a] B = benzil; D = DMAEMA = *N,N*-dimethylaminoethyl methacrylate.

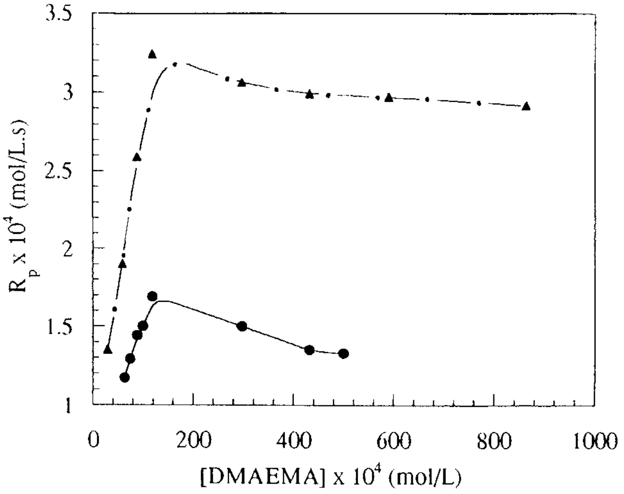


FIG. 1. Dependence of the MMA photopolymerization rate R_p on the DMAEMA concentration; [MMA] = 9.42 mol/L, (●) [benzil] = 0.001 mol/L, (▲) [benzil] = 0.1 mol/L.

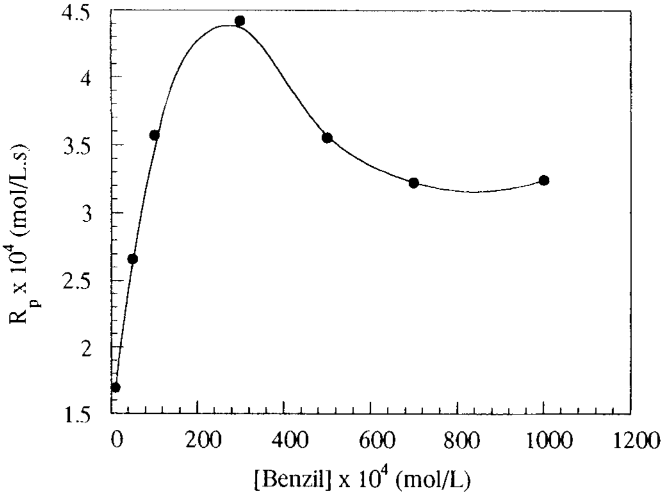


FIG. 2. Dependence of R_p on the benzil concentration; [MMA] = 9.42 mol/L, [DMAEMA] = 0.0119 mol/L.

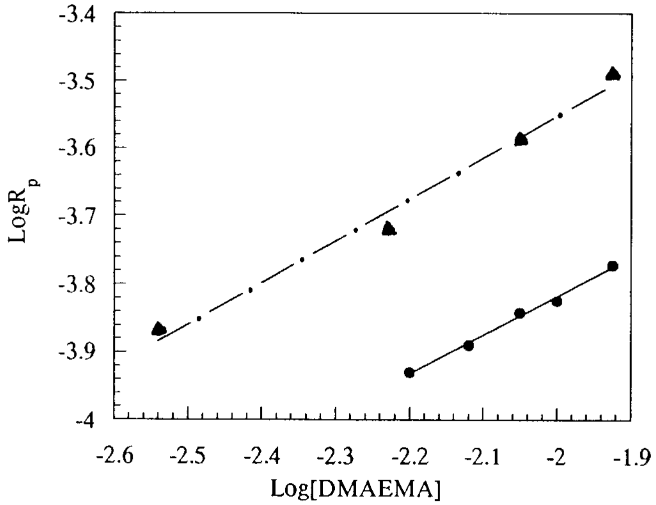


FIG. 3. Plots of log R_p vs log[DMAEMA]; (●) [benzil] = 0.001 mol/L, (▲) [benzil] = 0.1 mol/L.

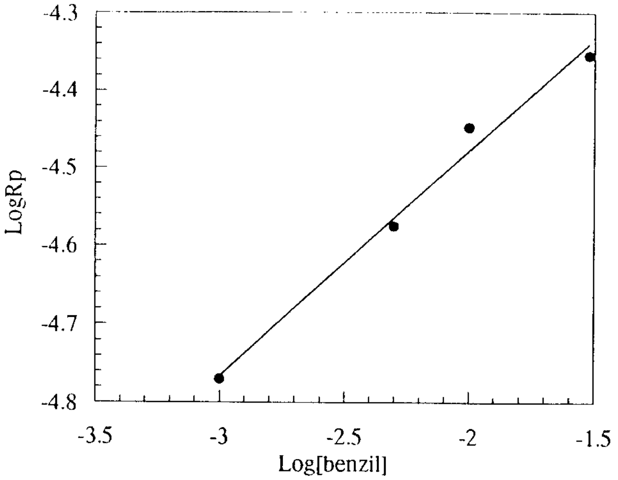


FIG. 4. Plot of log R_p vs log[benzil]; [DMAEMA] = 0.0119 mol/L.

The kinetic scheme for an ideal free radical photopolymerization is as follows.

Initiation:

$$\mathrm{I} \xrightarrow{h\nu} 2\mathrm{R}^{\cdot}$$

$$\dot{\mathrm{R}} + \mathrm{M} \xrightarrow{k_i} \mathrm{P}^{\cdot}_1$$

$$\mathrm{R}_i = 2\phi I_{\mathrm{abs}}$$

where ϕ = quantum yield of initiation (number of initiated chains per absorbed photon), I_{abs} = number of photons absorbed by the solution at a given wavelength of irradiation:

$$I_{\mathrm{abs}} = I_0(1 - e^{\epsilon l[\mathrm{I}]})$$

with I_0 = intensity of incident light, ϵ = molar extinction coefficient, l = optical path length, and [I] = initiator concentration. If the exponent of the above equation is small (which means dilute solutions in practice, since most absorption experiments are done with large ϵ), the exponential can be expanded, $e^x = 1 + x \ldots$, with only the leading terms retained to give [15–17]:

$$I_{\mathrm{abs}} = I_0 \epsilon l[\mathrm{I}]$$

Hence,

$$R_i = 2\phi I_0 \epsilon l[\mathrm{I}]$$

Propagation:

$$\mathrm{P}^{\cdot}_n + M \xrightarrow{k_p} {}^{\cdot}_{n+1}$$

Termination (bimolecular):

$$\mathrm{P}^{\cdot}_n + \mathrm{P}^{\cdot}_m \xrightarrow{k_t} \text{Polymer}, \qquad -d[\mathrm{P}^{\cdot}]/dt = 2k_t[\mathrm{P}^{\cdot}]^2$$

Assuming that radical reactivity is independent of radical size, application of the stationary state hypothesis ($R_i = R_t$) leads to the following expression for the concentration of polymer radicals:

$$[\mathrm{P}^{\cdot}] = (R_i/2k_t)^{1/2}$$

Then the polymerization rate is given by

$$R_p = -d[\mathrm{M}]/dt = k_p[\mathrm{M}][\mathrm{P}^{\cdot}] = k_p[\mathrm{M}](\phi I_0 \epsilon l[\mathrm{I}]/k_t)^{1/2}$$

Any modification of the initiation or termination mechanism which leads to a different expression for the concentration of polymer radicals also leads to values of initiator and monomer exponents other than 0.5 and 1, respectively (non-ideal polymerization). In this case the rate of polymerization is proportional to the x power of the initiator and the ω power of the monomer concentration ($R_p \approx [I]^x[M]^\omega$).

The termination mechanism of a polymerization can be elucidated by studying the dependence of the degree of polymerization ($\overline{P}_n$) on R_p. When the termination is bimolecular, $\overline{P}_n$ is given by the Mayo equation, which holds irrespectively of the nature of the initiation process:

$$\frac{1}{\overline{P}_n} = \frac{k_t}{k_p^2}\left[\frac{R_p(2+y)}{[M]^2(1+y)}\right]$$

where y is the ratio of the rate constant for termination by combination (k_{tc}) to the rate constant for termination by disproportionation (k_{td}). Taking into account that $y = 0.44$ at 20°C [18], this equation may be reduced to

$$\frac{1}{\overline{P}_n} = 1.69\frac{k_t}{k_p^2}\frac{R_p}{[M]^2}$$

In the studied polymerization system, when the concentration of benzil was kept constant and the concentration of DMAEMA was varied at low values, a plot of the reciprocal degree of polymerization $1/\overline{P}_n$ vs $R_p/[M]^2$ is linear (Fig. 5a). From the slope of this plot, the value of k_p^2/k_t was evaluated to be 0.33×10^{-2} mol/L·s. When the concentration of DMAEMA was kept constant and the concentration of benzil was varied at low values (Fig. 5b), this constant was found to be 0.38×10^{-2} mol/L·s. These values, compared with the literature value of k_p^2/k_t for an unretarded free-radical polymerization initiated by the conventional initiator AIBN at 20°C (0.26×10^{-2} mol/L·s [19]), indicate that termination of polymerization

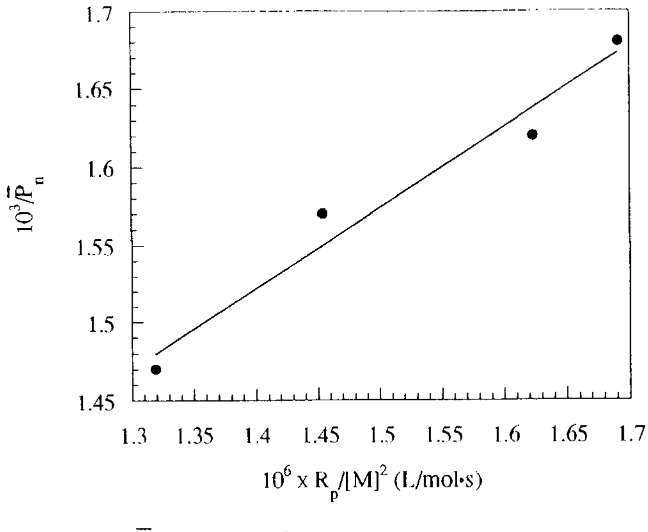


FIG. 5a. Plot of $1/\overline{P}_n$ vs $R_p/[M]^2$ at varied [DMAEMA] and constant [benzil] = 0.001 mol/L.

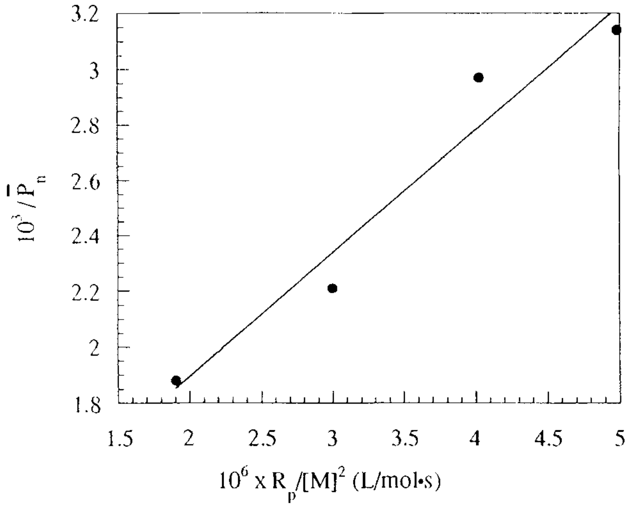


FIG. 5b. Plot of $1/\overline{P}_n$ vs $R_p/[M]^2$ at varied [benzil] and constant [DMAEMA] = 0.0119 mol/L.

is bimolecular and that other transfer or termination reactions induced by initiator or initiator components do not take place.

The values found in the present photopolymerization for the initiator exponent (0.3 with respect to benzil and 0.6 with respect to DMAEMA) indicate that the initiation mechanism is analogous to that described by the reactions shown in Scheme 1, where the actual initiator is the complex most probably formed by one molecule of benzil and two molecules of DMAEMA. Then the initiator concentration is proportional to the product [Benzil][DMAEMA]^2 and the value for the initiator exponent x ($R_p \approx \{[I] = [B][D]^2\}^x$) determined by varying the concentration of DMAEMA at a fixed concentration of benzil, is not the actual value ($x = 0.3$) but the apparent one ($2x = 0.6$). This result is in agreement with the finding of Sengupta et al. [7] that the excited benzil reacts with 2 moles of TEA.

The observed lower value of initiator order (0.3) than the usual value of 0.5 must be due to participation of the initiator in quenching reactions during the initiation process, which decrease its efficiency. Such unwanted side reactions have been reported generally to occur in the initiation process of vinyl polymerization induced by exciplexes [7, 20, 21].

At concentrations of DMAEMA higher than 0.0119 M, polymerization is retarded by DMAEMA (Fig. 1). The same effect was also observed at high concentrations of benzil (above 0.030 M). Bunbury [22], who studied the photolysis of benzil in neat triethylamine and mixtures of triethylamine with 2-propanol, found that the rate of benzil disappearance reaches a maximum and then declines as either the benzil concentration in triethylamine or the amine concentration in 2-propanol is increased. An excess of benzil will react with the α-amino radicals [3], causing a decrease in the efficiency of the initiator.

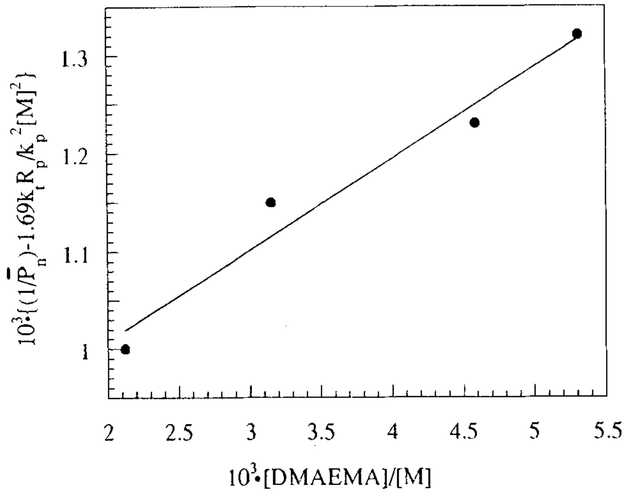
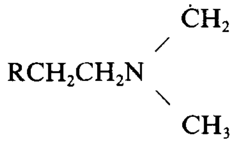


FIG. 6. Plot of $(1/\bar{P}_n) - 1.69k_tR_p/k_p^2[M]^2$ vs [DMAEMA]/[M]; [benzil] = 0.001 mol/L.

It is generally known that amines act as chain-transfer agents by the standard hydrogen abstraction mechanism. DMAEMA, which contains an amine group, could also act as a chain-transfer agent:

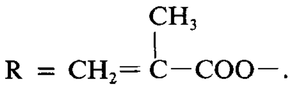
$$RCH_2CH_2N(CH_3)_2 + P_n^{\cdot} \xrightarrow{k_{tr}} RCH_2\dot{C}HN(CH_3)_2 + P_nH$$

or



$$RCH_2CH_2N\begin{matrix}\diagup \dot{C}H_2\\ \diagdown CH_3\end{matrix}$$

where



$$R = CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}COO{-}.$$

In order to evaluate the transfer constant of DMAEMA ($C_D = k_{tr}/k_p$), the Mayo equation was used in the following form for high concentrations of DMAEMA:

$$\frac{1}{\bar{P}_n} = 1.69\frac{k_t}{k_p^2}\frac{R_p}{[M]^2} + \frac{R_{tr}}{R_p}$$

where $R_{tr} = k_{tr}[P_n^{\cdot}][DMAEMA]$. Hence

$$\frac{1}{\bar{P}_n} - 1.69\frac{k_t}{k_p^2}\frac{R_p}{[M]^2} = C_D\frac{[DMAEMA]}{[M]}$$

A plot of the left-hand side of the above equation versus [DMAEMA]/[M] (Fig. 6) gave a straight line, the slope of which corresponds to the chain transfer constant of DMAEMA, $C_D = 0.093$ (at 20°C).

CONCLUSIONS

The benzil-DMAEMA combination was found to be an efficient photoinitiator for the bulk polymerization of MMA in air atmosphere without an induction period. The polymerization rate increases with benzil concentration <0.03 M and DMAEMA concentration <0.01 M; any further increase decreases the polymerization rate. At low concentrations of benzil and DMAEMA, the polymerization rate was proportional to the 0.3 power of the benzil concentration and the 0.6 power of the DMAEMA concentration. Based on these values, it is tentatively suggested that both carbonyl groups of benzil are excited and react with two molecules of DMAEMA to form a charge-transfer complex, which is the actual initiator. The decomposition of this complex gives α-amine radicals which then initiate polymerization. The initiator was also found to participate in unwanted quenching reactions which decrease its efficiency.

DMAEMA can also act as a chain-transfer agent. Its chain-transfer constant was found to be 0.093 at 20°C. The methacrylate moiety of DMAEMA can participate in the polymerization process and cause crosslinking.

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