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

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To cite this Article Sengupta, Pranab Kumar and Modak, Sadhan Kumar(1983) 'Photopolymerization of Methyl Methacrylate Using the Benzil-Dimethylaniline Combination as the Photoinitiator', Journal of Macromolecular Science, Part A, 20: 8, 789 — 805

To link to this Article: DOI: 10.1080/00222338308061399

URL: http://dx.doi.org/10.1080/00222338308061399

J. MACROMOL. SCI.–CHEM., A20(8), pp. 789-805 (1983)

Photopolymerization of Methyl Methacrylate Using the Benzil-Dimethylaniline Combination as the Photoinitiator

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ABSTRACT

Benzil (BZL)-dimethylaniline (DMA) exciplex interaction has been utilized to initiate the photopolymerization of methyl methacrylate at 40°C in bulk and in solution. Depending on the nature of the solvent used, the monomer exponent values varied between 0.47 to 2.76. Initiator exponent values were found to be 0.29 and 0.15 with respect to [BZL] and [DMA], respectively. A low value of k_p^2/k_t and the high initiator transfer constant values indicated significant initiator-dependent termination. The semipinacol radical formed during irradiation is thought to be mainly responsible for primary radical termination while the generated ion radicals are presumed to participate in degradative initiator transfer.

INTRODUCTION

It is now well established that photoexcited aromatic carbonyl compounds under appropriate conditions may induce free radical vinyl

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0022-233X/83/2008-0789$3.50/0

polymerization [1, 2]. The photoinitiation occurs through the radical generation process involving the excited carbonyl compound and the monomer. This involvement with monomer may be a direct addition, a hydrogen abstraction, an energy transfer, or an electron transfer to the monomer. Alternatively, the photoexcited carbonyl compound as such may undergo simple photofragmentation to yield radicals [3].

It has been observed that in the presence of some additives, particularly amines, the photoinitiating activity of the ketone is enhanced [4-7] and this has been shown to occur through exciplex formation [5]. A greater efficiency of intersystem crossing resulting from the exciplex interaction of triplet excited ketone with ground state amine leads to an efficient photoinitiation system. It is thus obvious that neither all types of ketones nor hydrogen additives are equally effective. A detailed investigation is, therefore, necessary to assess the relative effectiveness of various ketone-amine combination systems based on their photochemical and photophysical characteristics.

During our search of the literature we found that there is practically no detailed information on the effect of various amines on benzil and benzoin systems although some of these combination systems have already found important industrial photocuring applications. It was therefore considered to be of some interest to investigate the relative effectiveness of some of these systems, and in this paper we report some kinetic and mechanistic aspects of the photoinduced polymerization of methyl methacrylate (MMA) using benzil (BZL)-dimethylaniline (DMA) combination system. It is interesting to mention that although benzil is widely used as a good photoinitiator, opinions differ as to its exact mode of photoinitiation [3, 8, 9].

EXPERIMENTAL

Materials

MMA was made inhibitor-free and then distilled under reduced pressure. Benzil was twice recrystallized from alcohol and dried under vacuum. Dimethylaniline was purified by keeping it overnight with KOH and then distilling it under nitrogen atmosphere. Benzene (thiophene-free) was dried over metallic sodium and then distilled.

All other solvents were purified by their standard methods of purification.

Polymerization Procedure

The polymerization of MMA in bulk and in solution was studied dilatometrically under irradiated conditions by using a dilatometer made from borosilicate glass. The light source was a high-pressure mercury vapor lamp, 125 W (Philips India Ltd). Polymers formed at low conversions (10%) in the dilatometer were removed and isolated by precipitation with methanol followed by drying at 45°C under vacuum.

Molecular Weight Determination

Molecular weights ($\overline{M}_n$) of the polymers were obtained from viscosity measurements in benzene solution at 30 ± 0.01°C using the following relationship [10]:

$$[\eta] = 8.69 \times 10^{-5} \overline{M}_n^{0.76} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity in dL/g.

RESULTS AND DISCUSSION

In the presence of the BZL-DMA initiator system, no polymerization of MMA was observed in the dark at 40° C. The polymerization of MMA was, however, readily induced in the presence of light with an inhibition period of the order of 0 to 20 min. The polymerization was also inhibited in the presence of hydroquinone. The results of photopolymerization experiments of MMA using different concentrations of DMA and BZL are presented in Table 1. Rates of polymerization, R_p, were calculated from the initial linear zones of conversion-time plots. The dependence of R_p on [DMA] and [BZL] has been shown from their respective logarithmic plots (Figs. 1a and 1b), and the corresponding reaction orders are 0.15 and 0.29, respectively. A plot of log R_p vs log ([DMA] [BZL]) corresponds to an order of 0.25 (Fig. 1c). All these values are substantially lower than the usual order, viz. 0.5, for normal bimolecular termination, and signify some kind of initiator-dependent termination.

k_p^2/k_t Value

This kinetic parameter at 40°C was evaluated from the slope of the plot of $1/\overline{P}_n$ vs $R_p/[M]^2$ (Fig. 2, Table 1) following the Mayo equation [11] and was found to be 0.47×10^{-2} L/mol • s. The relatively low value implies termination or transfer by the initiator components and presumably by primary radicals formed during irradiation.

Initiator Transfer

The values of initiator transfer constants, C_{DMA} and C_{BZL}, are obtained by using the Mayo equation in the following form:

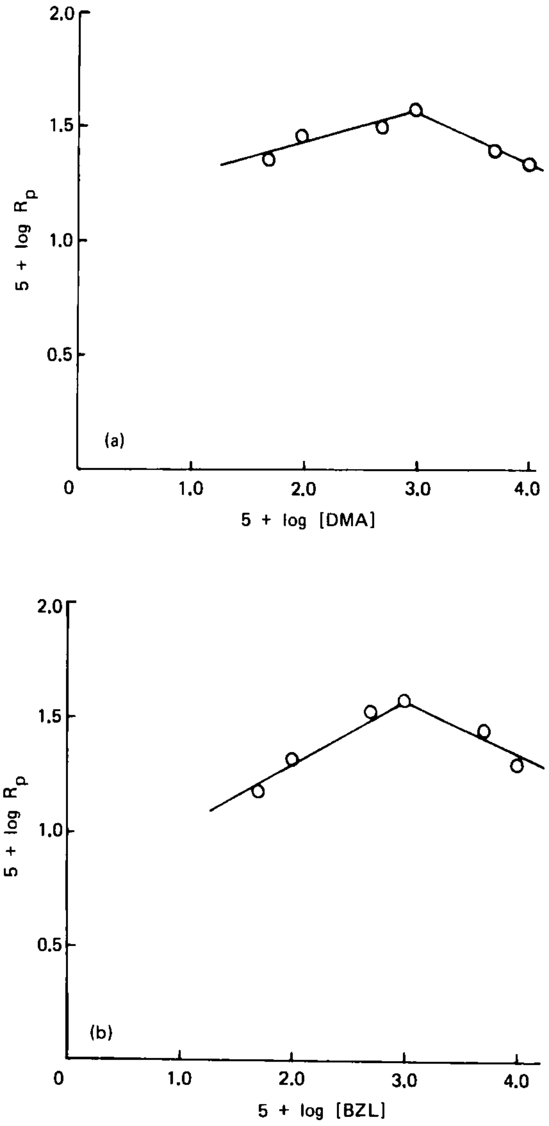


FIG. 1. Photopolymerization of MMA at 40°C using the BZL-DMA combination as the initiator.

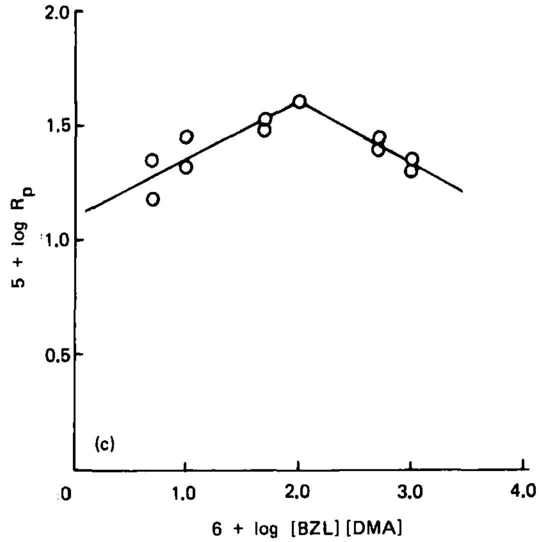


FIG. 1 (continued)

$$\frac{1}{\overline{P}_n} - 1.85\frac{k_t}{k_p^2}\frac{R_p}{[M]^2} = C_M + C_{BZL}\frac{[BZL]}{[M]} + C_{DMA}\frac{[DMA]}{[M]} \qquad (2)$$

when the left-hand side of Eq. (2) was plotted against [DMA]/[M] at fixed [BZL] (Fig. 3a) and [BZL]/[M] at fixed [DMA] (Fig. 3b). The values of C_{DMA} and C_{BZL} were found to be 0.146 and 0.173, respectively. Although these are only approximate values, nevertheless they are quite appreciable compared to the low transfer constants normally observed in typical free radical initiation. These relatively higher values of transfer constants substantiate the lower value of k_p^2/k_t obtained in this particular system.

Activation Energy

The apparent activation energy E_a ($E_a = (E_p - E_t)/2$), calculated from the slope of the Arrhenius plot (Fig. 4), is found to be 4.39 kcal/mol (18.44 kJ/mol). This is in the order of typical photopolymerization systems involving a temperature-independent initiation step.

TABLE 1. Photopolymerization of MMA in Bulk at 40°C Using the BZL-DMA Combination as the Initiator

$[BZL] \times 10^4$ mol/L	$[DMA] \times 10^4$ mol/L	$R_p \times 10^5$ mol/L·s	$\frac{R_p}{[M]^2} \times 10^6$	$[\eta]$ (dL/g)	$\frac{1}{\overline{P}_n} \times 10^3$	Initiator exponent	$\frac{k_p^2}{k_t} \times 10^2$ L/mol·s
100	1000	22.0	2.576	0.4043	1.50	0.15	0.47
100	500	25.0	2.927	0.3743	1.65		
100	100	38.3	4.484	0.3171	2.04		
100	50	32.0	3.747	0.3690	1.68		
100	10	29.0	3.395	0.4086	1.47		
100	5	23.0	2.693	0.4931	1.15		
1000	100	20.0	2.342	0.2806	2.42	0.29	
500	100	28.0	3.290	0.2631	2.62		
100	100	38.3	4.484	0.3171	2.04		
50	100	33.3	3.899	0.3598	1.74		
10	100	20.8	2.435	0.5010	1.12		
5	100	15.0	1.779	0.6372	0.82		

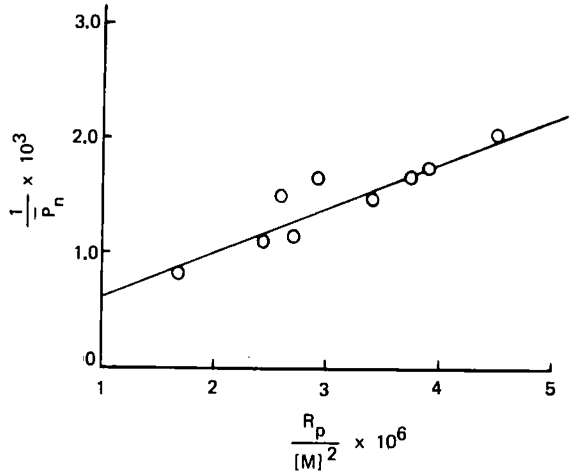


FIG. 2. Photopolymerization of MMA at 40°C using the BZL-DMA combination as the initiator.

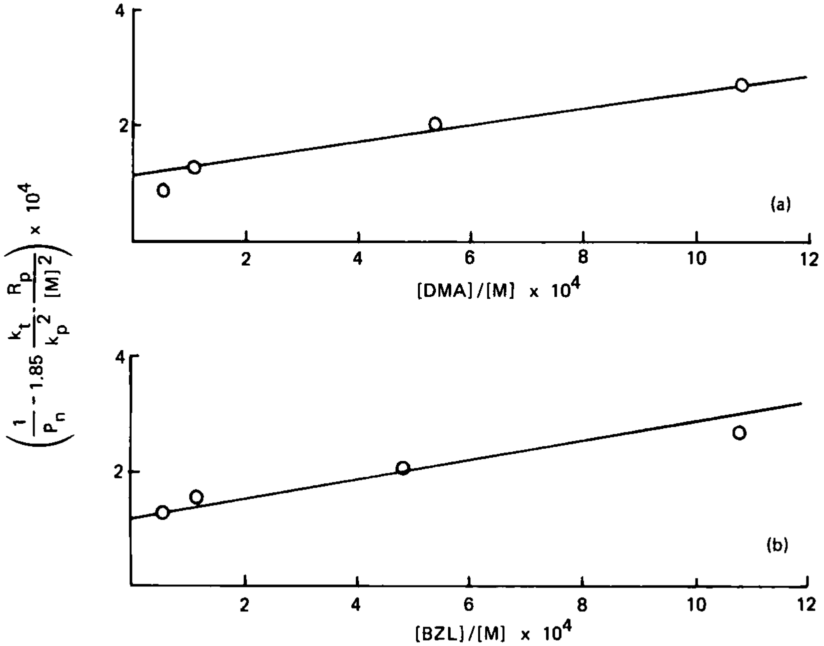


FIG. 3. Photopolymerization of MMA at 40°C using the BZL-DMA combination as the initiator.

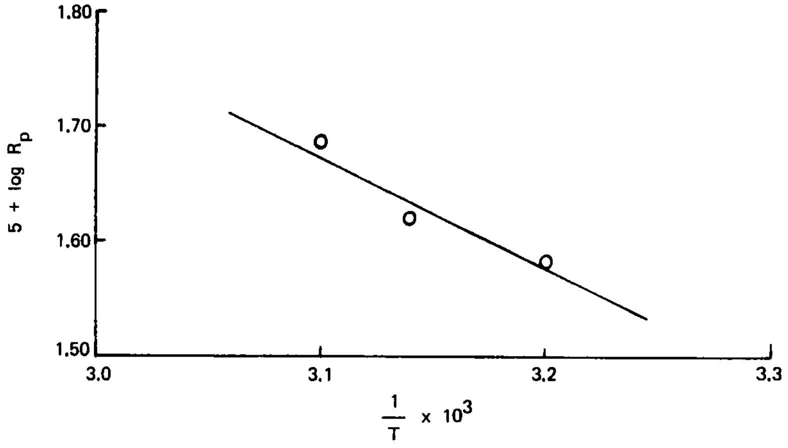


FIG. 4. Effect of temperature on the photopolymerization of MMA using the BZL-DMA combination as the initiator.

Solvent Effect

The photopolymerization experiments were also performed in the presence of few solvents such as benzene, carbon tetrachloride (CCl_4), isopropanol (IPA), tert-butanol (t-BuOH), dimethylformamide (DMF), and tetrahydrofuran (THF). The initiator concentration was kept fixed in all the experiments ([BZL] = 1×10^{-2} mol/L, [DMA] = 1×10^{-2} mol/L). Monomer orders calculated from the slope of the respective plots of log R_p vs log [M] were found to lie between 0.47 to 2.76 (Table 2) depending on the nature of the solvent used. This solvent dependency on the monomer order may be analyzed by considering their participation in the radical generation/initiation process. The overall radical generation (initiation) process where the solvent (S) influences the initiation step may be written as

$$\text{I} \xrightarrow{k_1} \text{primary radicals} \tag{3}$$

$$\text{I} + \text{S} \xrightarrow{k_2} \text{primary radicals} \tag{4}$$

where I is the initiator.

The rate of initiation is

$$R_i = k_1[I] + k_2[I][S] \tag{5}$$

TABLE 2. Variation of the Rate of Polymerization (R_p) with Monomer Concentration (MMA) Using the BZL-DMA Combination as the Initiator at 40°C: [BZL] = 1×10^{-2} mol/L, [DMA] = 1×10^{-2} mol/L

Solvents	[M] (mol/L)	$R_p \times 10^5$ mol/L·s	log [M]	5 + log R_p	Monomer exponent
Benzene	9.238	38.3	0.9657	1.5832	1.12
	8.314	33.3	0.9198	1.5237	
	7.390	29.1	0.8686	1.4639	
	6.466	25.2	0.8106	1.4014	
	5.543	21.9	0.7437	1.3404	
CCl_4	9.238	38.3	0.9657	1.5832	0.47
	8.314	37.0	0.9198	1.5682	
	7.390	34.0	0.8686	1.5315	
	6.466	33.0	0.8106	1.5185	
	5.543	30.0	0.7437	1.4771	
DMF	9.238	38.3	0.9657	1.5832	1.15
	8.314	32.4	0.9198	1.5105	
	7.390	28.3	0.8686	1.4518	
	6.466	25.0	0.8106	1.3979	
	5.543	21.8	0.7437	1.3400	
THF	9.238	38.3	0.9657	1.5832	1.07
	8.314	32.5	0.9198	1.5119	
	7.390	29.1	0.8686	1.4639	
	6.466	25.0	0.8106	1.3979	
	5.543	22.2	0.7437	1.3464	
IPA	9.238	38.3	0.9657	1.5832	2.76
	8.314	23.1	0.9198	1.3636	
	7.390	16.6	0.8686	1.2201	
	6.466	10.9	0.8106	1.0374	
	5.543	7.5	0.7437	0.8751	
t-BuOH	9.238	38.3	0.9657	1.5832	2.41
	8.314	31.2	0.9198	1.4942	
	7.390	21.6	0.8686	1.3345	
	6.466	16.2	0.8106	1.2095	

Assuming, for simplicity, that the termination process is mainly bimolecular and that no initiator dependent termination is involved, then

$$R_i = k_1[I] + k_2[I][S] = 2\frac{k_t}{k_p^2}\frac{R_p^2}{[M]^2}$$

or

$$2\frac{k_t}{k_p^2}\frac{R_p^2}{[I][M]^2} = k_1 + k_2[S] \qquad (6)$$

where

$$[I] = [BZL][DMA]$$

When a plot of the left-hand side of Eq. (6) against [S] was made for various solvents (Fig. 5), linearity was observed over a large range of [S]. This reasonably substantiates the above general approach to describe radical generation or chain initiation. A significant positive slope for the plot involving CCl_4 is obtained, which indicates that the rate-enhancing effect of this solvent is due to its active participation in the initiation step. Benzene, DMF, and THF appear to exhibit practically inert diluent effects. However, significant negative slopes for the respective plots in IPA and t-BuOH are obtained which indicate the rate-retarding effect of these solvents. This is quite expected in view of the fact that CCl_4 can effectively produce $^{\bullet}CCl_3$ to enhance the initiation rate in inert atmosphere and that the photolysis of ketones in CCl_4 solution do produce such radicals as has already been reported [12]. The rate-retarding effects of alcohols (IPA and t-BuOH) may be explained on the basis of hydrogen abstraction from these solvents by benzil, resulting in the production of a radical $Ph\dot{C}(OH)COPh$ which is a good terminating species [13, 14] and a corresponding solvent-derived radical which is a poor initiating species. From the quantum yield measurements it has been established [15-18] that increasing solvent polarity decreases the facility for intersystem crossing and simultaneously increases the quantum yield for fluorescence. Thus for solvents such as benzene and cyclohexane, triplet yields are near unity, thereby showing the maximum triplet state activity. On the other hand, in solvents such as alcohols, triplet yields are substantially less than unity with a constant increase in quantum yield of fluorescence.

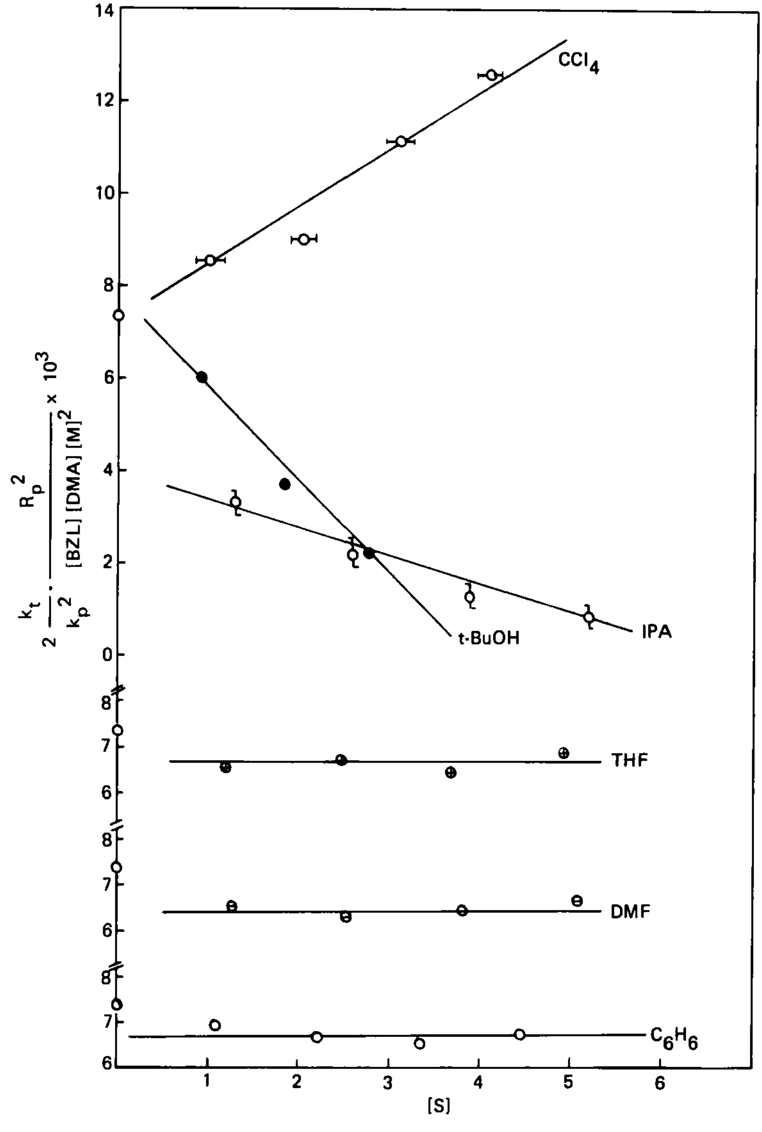
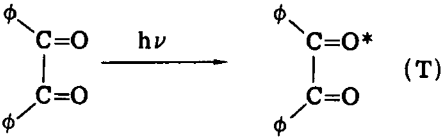


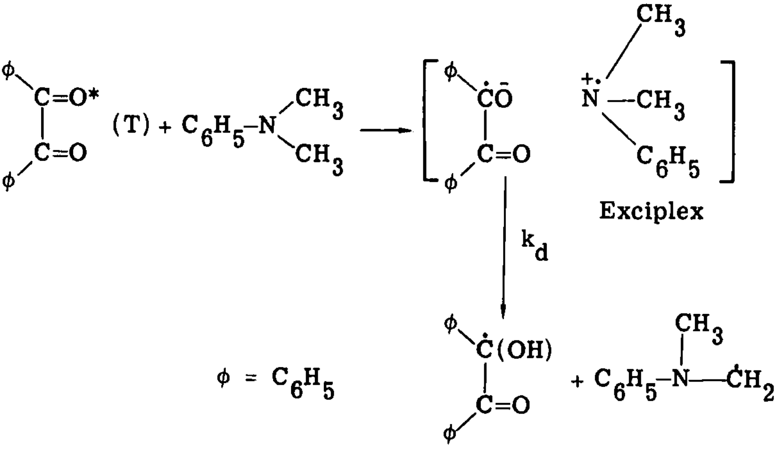
FIG. 5. Photopolymerization of MMA in the presence of solvents at 40°C using the BZL-DMA combination as the initiator.

Mechanism of Photoinitiation

The photopolymerization of MMA with the BZL-DMA initiator system was found to be inhibited in the presence of a low concentration of hydroquinone. The polymerization thus appears to take place by a radical mechanism. There are several reports [4-7] on the photoreduction of aromatic carbonyl compound by various amines, in the presence of various solvents/additives, and various sequences of reactions including photoexcitation of aromatic ketone and their interactions with ground state additives such as amines to form exciplex and the subsequent decomposition of exciplex to form radicals recognized to be important in such systems. In view of the above facts, the following simplified sequence of reactions may be considered to describe the overall radical generation process in the present photopolymerization system.



(7)



(8)

(9a) (9b)

Thus triplet excited benzil and ground state amine undergo a charge-transfer type of interaction to form an exciplex (8) which subsequently decomposes to the ketyl (9a) and amine (9b) radicals via a proton transfer reaction as shown. The semipinacol radical (9a) thus produced as an intermediate during the photoreduction of BZL may cause significant chain termination and is manifested by the lower exponent values obtained earlier.

Initiator-Dependent Termination

It has already been pointed out that a low value of k_p^2/k_t and a higher transfer constant in the BZL-DMA system may be associated with some initiator-dependent termination. Two types of termination may be considered, viz. primary radical termination and degradative initiator transfer.

Primary radical termination:

$$M^{\circ} + R^{\bullet} \xrightarrow{k_{prt}} \text{polymer product} \tag{10}$$

Termination via degradative initiator transfer (assuming little reinitiation effect):

$$M^{\bullet} + I \xrightarrow{k_t'} \text{polymer product (chain inactive by-product)} \tag{11}$$

Analysis of Primary Radical Termination Effect

The primary radical termination effect in the absence of any degradative initiator transfer process may be evaluated by using the equation derived by Deb and Meyerhoff [19] in the following form:

$$\log \frac{R_p^2}{[BZL][DMA][M]^2} = \log \frac{fk_dk_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_ik_p} \frac{R_p}{[M]^2} \tag{12}$$

The left-hand side of Eq. (12) was plotted against $R_p/[M]^2$ at fixed [BZL] (Fig. 6a) and at fixed [DMA] (Fig. 6b). The plots gave straight lines with negative slopes, thereby indicating the measurable primary radical termination effect. The values of the parameter k_{prt}/k_ik_p were obtained from the slope of each plot, and they are 2.5×10^6 and 2.5×10^5 mol·s/L, respectively.

Analysis of Degradative Initiator Transfer with Little Reinitiation Effect

Assuming the steady-state condition, a simple kinetic analysis leads to the following expression:

$$2 \frac{k_t}{k_p^2} \frac{R_p^2}{[M]^2[BZL][DMA]} = 2\phi\epsilon I_0 - \frac{k_t'}{k_p} \frac{R_p}{[M]} \tag{13}$$

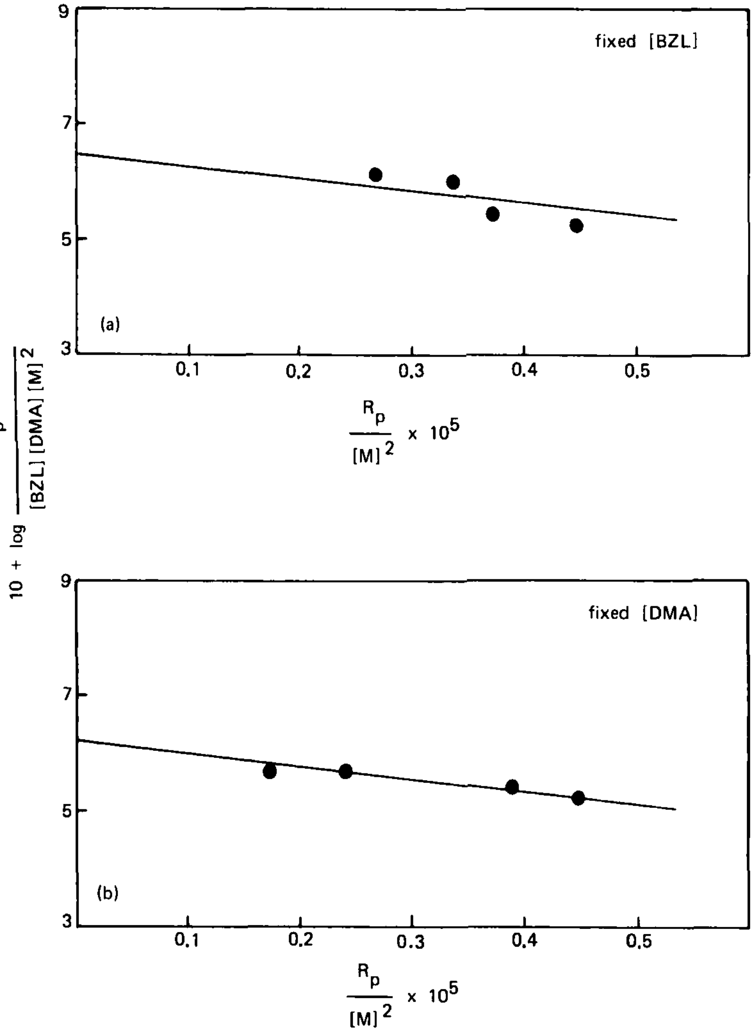


FIG. 6. Analysis of primary radical termination effect on the photopolymerization of MMA at 40°C using the BZL-DMA combination as the initiator.

Plots of the left-hand side of Eq. (13) against $R_p/[M]$ using a fixed [BZL] and a fixed [DMA], respectively, yield straight lines with negative slopes which give clear evidence for degradative initiator transfer (Figs. 7a and 7b). The values of k_t'/k_p as calculated from the slopes of the plots are 3.2×10^3 and 1.38×10^3, respectively.

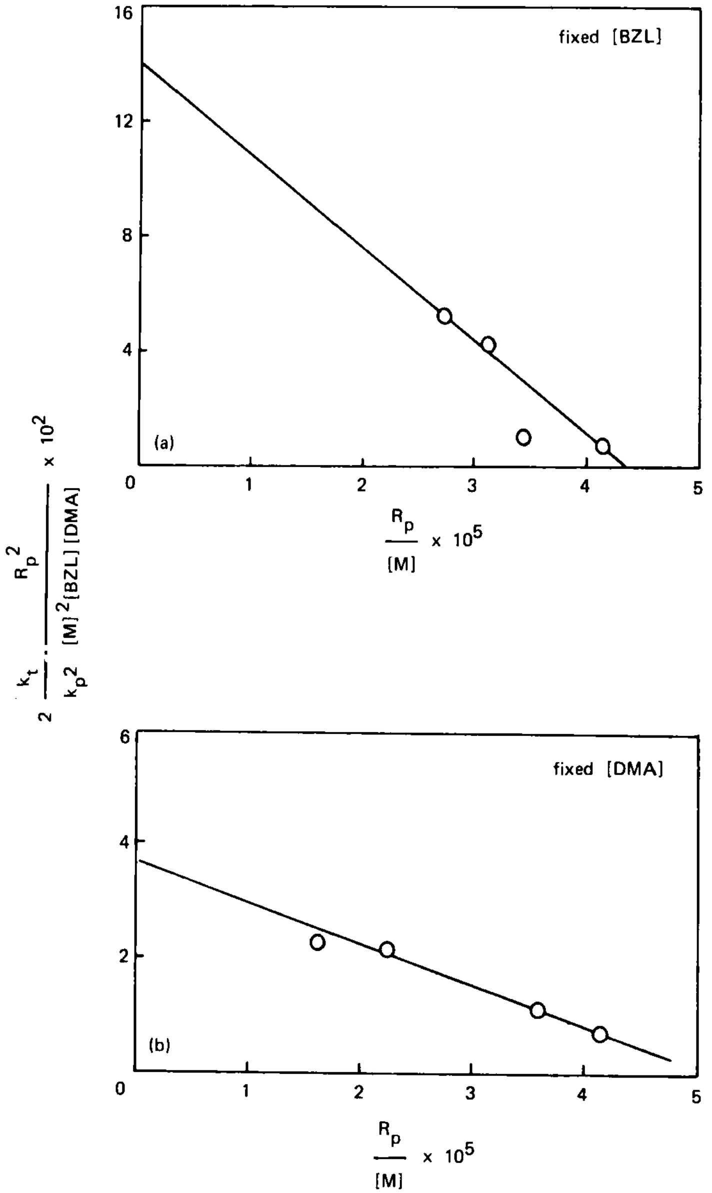


FIG. 7. Analysis of degradative initiator transfer effect (with little reinitiation) on the photopolymerization of MMA at 40°C using the BZL-DMA combination as the initiator.

Mechanism of Initiator-Dependent Termination

Excited benzil, as such, may participate in the quenching or energy wastage mechanism. Alternately, singlet and triplet exciplexes ($BZL^{\cdot -}R_3N^{\cdot +}$), which are produced, may yield chemical products directly from the triplet exciplex or via a pair of ion radicals ($BZL^{\cdot -}$) ($R_3N^{\cdot +}$). These types of reactions have already been proposed in systems containing fluorenone-amine as the photoinitiator for the photopolymerization of MMA [5]. It is also known that MMA monomer itself may participate in the deactivation process in the above system. There are reactions occurring to deactivate intermediate exciplexes prior to radical formation and to scavange radicals once they are formed.

In the case of the photopolymerization of MMA using a photoinitiator, Bunbury [13, 14] has shown that photoexcited benzil can abstract hydrogen from good hydrogen donor solvents to form $Ph\dot{C}(OH)COPh$ and a solvent-derived radical. The former radical is known to be a good terminating species for polymer radicals. In the absence of any solvent, when MMA is polymerized with benzil, a low initiation efficiency results due to the participation of such radicals which are poor initiating species. In view of the above facts it is reasonable to assume that in the BZL-DMA system the semipinacol radical derived from benzil is mainly responsible for primary radical termination. It is known that in the case of photoreduction of benzophenones with amines [20] there exist both ion radical pairs and free radicals. In the present system, these ion radicals, derived from amines, may presumably participate in the degradative initiator transfer process with little reinitiation effect.

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Accepted by editor March 30, 1983
Received for publication May 1, 1983