A Study of Sensitizer Systems for Photoinitiated Polymerization

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A Study of Sensitizer Systems
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ABSTRACT

The polymerization of unsaturated monomers can be initiated
by ultraviolet radiation. This method of initiation has been used
to form polymers, to graft polymerize monomers onto existing
polymers, and to crosslink prepolymer systems. These reac-
tions usually require the presence of photosensitizer species in
order to take place and electron donors, such as tertiary amines,
have been shown to increase the rate of reaction. Many of these
sensitizer systems have been reported for a large variety of
polymerizations, but there appears to have been little attempt
to relate activity to chemical structure using comparable condi-
tions. The present study has statistically evaluated the activity
of a number of sensitizers and amines over a range of concen-
trations by use of methyl acrylate as a common monomer. Other
monomers have also been studied. Polymerization rates have
been measured using refractometry. Relatively low intensity
lamps have been used for irradiation to enable the polymerizations
to proceed at a slow enough rate for measurements to be con-
veniently made. The results could be extrapolated to application
of high intensity ultraviolet radiation as used in rapid polymeriz-
ing formulations.

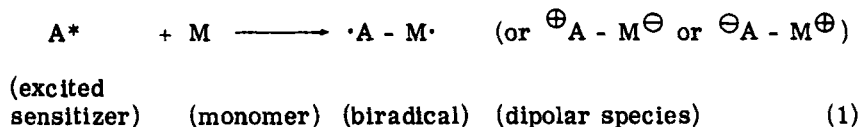*Present address: Nonporite Pty. Ltd., Melbourne, Australia.

INTRODUCTION

Polymerization of substrates by ultraviolet radiation has been demonstrated to have many applications, some of which have been used commercially in recent years. The main uses are in the grafting onto other polymeric materials [1], curing of inks, coatings, filler pastes, and paper lacquers [2, 3], and producing photoresist images on printing plates and electronic integrated circuitry [4]. These systems have the advantage that they do not require solvents to be evaporated with subsequent environmental effects and they can be made to react very rapidly.

These polymerizations can be classified into two types: photopolymerization, where monomers add via step-growth polymerization induced by ultraviolet radiation, and photoinitiated polymerization, where a photoinitiator or sensitizer is required for rapid polymerization via a chain growth mechanism initiated by ultraviolet radiation. The present paper will be concerned with the second mechanism.

Photoinitiators can be classified into the following six basic classes [5]:

Direct addition of excited sensitizer to monomer to form a biradical or dipolar species:

$$A^* \quad + M \longrightarrow \cdot A - M \cdot \quad (\text{or } {}^{\oplus}A - M^{\ominus} \text{ or } {}^{\ominus}A - M^{\oplus})$$

$$\begin{array}{llll}
\text{(excited} & & & \\
\text{sensitizer)} & \text{(monomer)} & \text{(biradical)} & \text{(dipolar species)} \qquad (1)
\end{array}$$

Excited triplet sensitizer excites monomer to triplet state with the evolution of some energy.

$$A(T_1) + M(S_0) \longrightarrow A(S_0) + M(T_1) + \text{energy} \qquad (2)$$
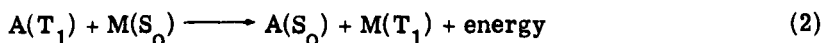
Excited photosensitizer cleaves to form two radicals of which one or both may initiate polymerization:

$$(A - B)^* \longrightarrow A \cdot + B \cdot \qquad (3)$$

Excited sensitizer abstracts hydrogen from another molecule to form two radicals and usually one of these initiates polymerization.

$$A^* + RH \longrightarrow \cdot AH + R \cdot \qquad (4)$$

Electron transfer produces a pair of ion-radicals:

$$A^* + M \longrightarrow A^{\oplus \cdot} + M^{\ominus \cdot} \text{ (or } A^{\ominus \cdot} + M^{\oplus \cdot}) \tag{5}$$

Photoexcitation of charge transfer bands of inorganic salts:

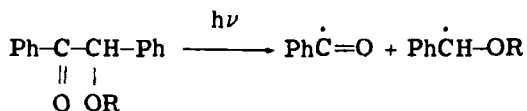$$A^{\oplus *} + X^{\ominus} \longrightarrow A^{\cdot} + X^{\cdot} \tag{6}$$

Only mechanisms (3), (4), and (5) have been found to be of commercial use. The study described in this paper is also restricted to these three mechanisms.

Most singlet radicals are relatively short-lived, and therefore their chances of initiating polymerization are limited. However, many triplet radicals are sufficiently long-lived to efficiently initiate polymerization. Under ultraviolet irradiation, a molecule can be excited from the ground state to the first singlet state, $S_0 \longrightarrow S_1$. However, intersystem crossing to the triplet state, $S_1 \longrightarrow T_1$, is spin-forbidden. This accounts for the slow polymerization of pure monomers irradiated by ultraviolet light. By incorporating a sensitizer which can efficiently undergo the $S_1 \longrightarrow T_1$ transition, the polymerization can be caused to proceed rapidly since the sensitizer can transfer its triplet energy to the monomer, exciting it to the long-lived radical triplet state [6].

The most important class of photoinitiators are benzoin and its alkyl ethers. These undergo Norrish type 1 cleavage [7]:

$$\underset{\underset{\text{O} \ \text{OR}}{\overset{\| \quad |}{}}}{\text{Ph}-\text{C}-\text{CH}-\text{Ph}} \xrightarrow{h\nu} \text{Ph}\overset{\cdot}{\text{C}}{=}\text{O} + \text{Ph}\overset{\cdot}{\text{C}}\text{H}-\text{OR}$$

Another important class of photoinitiators involves photoinitiated hydrogen transfer. These are usually aromatic carbonyl compounds, benzophenone being the most common. Without a proton donor the initiation is very slow or may not occur. This may involve initial formation of a charge-transfer complex [8]. Amines can accelerate benzophenone photoinitiated polymerizations due to the formation of charge transfer complexes between the amine and the benzophenone. It has been found that tertiary amines, especially hydroxyalkyl tertiary amines, accelerate photoinitiation by benzophenone to the greatest extent [9].

The photoinitiation of a wide variety of monomers has been studied,

TABLE 1. Interaction between Benzophenone and Triethylamine[a]

Level of benzophenone (%)	Level of triethylamine (%)	Replications rate (mole/ $dm^3 \times 10^3$)		Sum of replications
		1	2	
0.5	0.5	11.50	11.50	23.00
	2.0	10.00	10.00	20.00
	4.0	7.36	7.29	14.65
1.0	0.5	8.12	8.01	16.13
	2.0	9.08	9.01	18.09
	4.0	6.73	6.57	13.30
2.0	0.5	3.66	3.68	7.34
	2.0	7.70	7.51	15.21
	4.0	5.38	5.11	10.49

[a] Analysis of data: effect of benzophenone, $F(2,9) = 2868 \gg F_{0.01}$ = 8.02; effect of triethylamine, $F(2,9) = 1037 \gg F_{0.01}$ = 8.02; interaction between benzophenone and triethylamine, $F(4,9)$ 588 $\gg F_{0.01}$ = 6.42; residual standard deviation in results = 0.09 which corresponds to a 0.9% error in the data.

viz, acrylates, methacrylates, acrylonitrile, styrene, and vinyl acetate [10]. Acrylates show the most rapid polymerization and consequently these have been incorporated in a number of photocurable oligomers. Styrene forms charge-transfer complexes with amines which have been shown to initiate styrene photopolymerization [11].

Two other variables are the wavelength of the radiation and the influence of oxygen. Wavelength needs to be chosen to coincide with absorption of the initiator but to differ from absorptions of other components of the system. Oxygen will retard the polymerization reaction. The main practical method to exclude oxygen has been to include an incompatible wax in formulations. The wax migrates to the surface creating a barrier between the atmosphere and the polymerizing medium. Studies have been performed by using this method, freeze-thaw vacuum techniques, and an inert atmosphere or no exclusion of oxygen.

The variables discussed have been studied using a range of different techniques which makes it difficult to compare their effects

overall. This study aims to measure photoinitiated polymerization rates by using a consistent technique and conditions so as to enable statistical evaluation of the performance of components of the systems and to determine the optimum concentrations for rapid polymerizations. It is hoped that the results will enable a systematic approach to the choice of components for formulation application.

RESULTS AND DISCUSSION

Polymerization rates were measured by refractometry and for the initial part of the project methyl acrylate was used with no other diluent.

Measurements with different concentrations of benzophenone and triethylamine (Table 1) demonstrate statistically the interaction between the two initiators. The precision of the rate determinations was assessed at 0.9% from the analysis of variance residual. Benzophenone and triethylamine each showed little (0.1% after 10 min) or no polymerization when used separately. The initiation in this case is said [5] to proceed by a hydrogen abstraction from the amine by an excited benzophenone molecule. Only the amine radical initiates polymerization; the benzophenone is only capable of acting as a chain terminator.
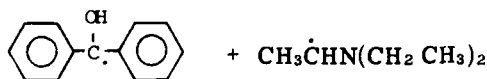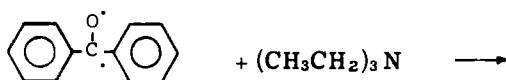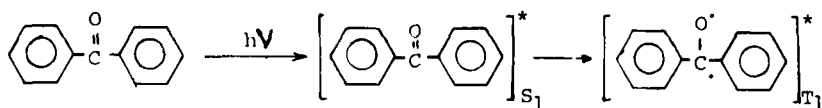
Both the benzophenone and triethylamine concentrations led to a maximum rate at a fairly low concentration (results of Table 2, Figs. 1 and 2).

TABLE 2. Effect of Benzophenone and Triethylamine Concentration
on Rate

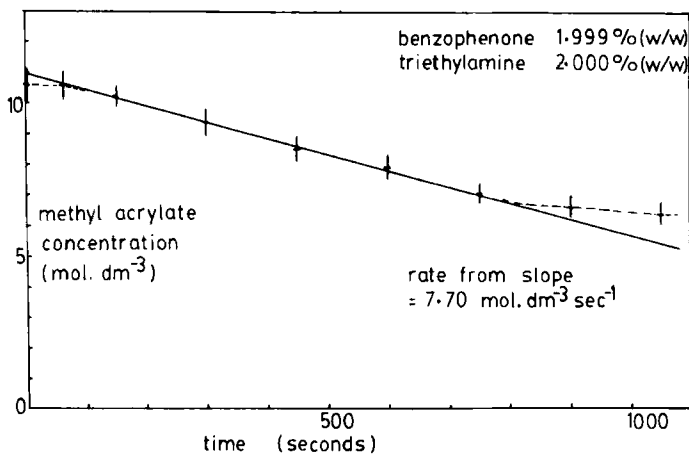| Trimethylamine (% w/w)	Extent of polymerization at various benzophenone concentrations (%)						
	0.050 (%)	0.10 (%)	0.20 (%)	0.40 (%)	0.50 (%)	1.00 (%)	2.00 (%)
0.050					3.8		
0.10					14.0		
0.20					37.9		
0.40					55.7		
0.50	35.2	51.0	62.7	60.4	56.0	39.0	21.0
2.00					51.0	50.3	37.8
4.00					42.0	40.6	31.2

FIG. 1. A typical rate plot.

Thus speed of cure is not assured by increasing photoinitiator concen-
tration yet the concentration for the optimum rate may not give com-
plete cure. Such a problem may be overcome by using two initiators,
one to achieve rapid cure and the other to achieve complete curing by
either photoinitiation or a subsequent thermal cure. It is also desir-
able to keep the concentration of benzophenone initiators low since a
byproduct is benzopinacol, formed by coupling of two diphenylmethanol
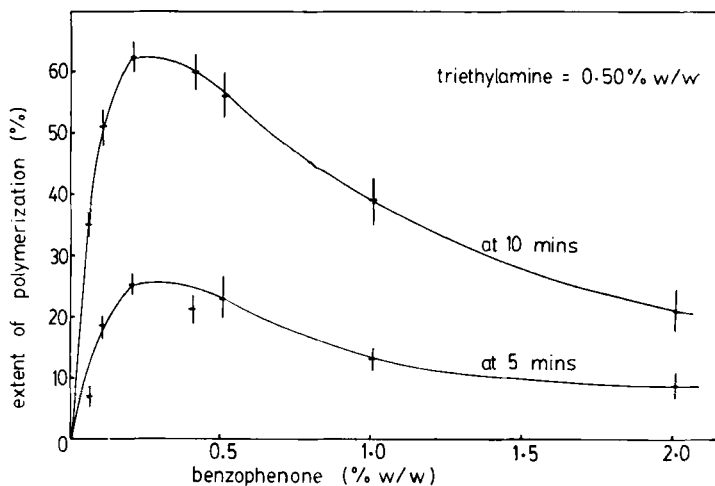radicals; yellowing of the polymer is also a problem.
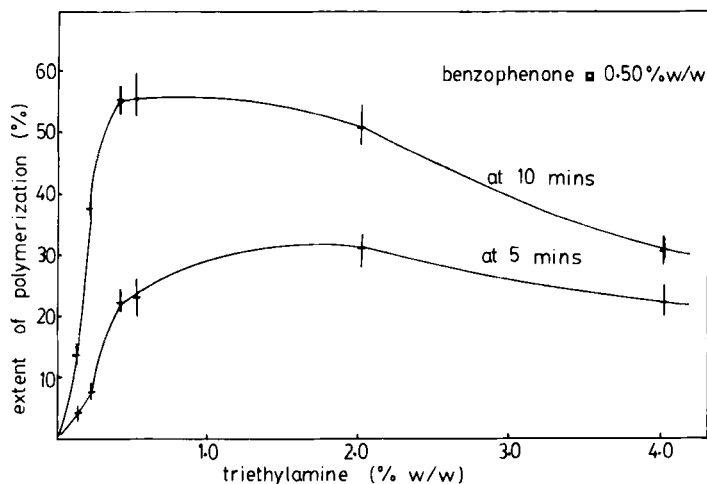
FIG. 2. Optimization of benzophenone.

FIG. 3. Optimization of triethylamine.

Comparison of the activity of photoinitiators indicates that those which readily undergo a scission reaction to produce two radicals give greatest conversion. Thus benzoin and its ethers and benzil diethyl ketal are the most effective initiators tested. Benzoin methyl ether was more effective than the isopropyl ether. Benzil diethyl ketal was the most active initiator tested. In these experiments no

TABLE 3. Activity of Photoinitiators with Methyl Acrylate

Photoinitiator[a]	Conversion at 10 min (%)
Benzophenone	0.1
Benzophenone + (triethylamine)[b]	62.7
Fluorenone	0.2
Benzoin	15.8
Benzoin methyl ether	59.8
Benzoin isopropyl ether	33.5
Benzil	0.2
4,4'-Bis(dimethylamino)benzophenone	3.9
Benzil diethyl ketal	80.3

[a]1.57 ± 0.01 mole/dm$^3 \times 10^2$.
[b]4.64 mole/dm$^3 \times 10^2$.

amine was included. Subsequent experiments will include various tertiary amines as well as mixed initiators.

At this stage only a preliminary study of monomers has been performed. The results follow the expected trend that acrylates are faster than methacrylates or vinyl compounds. It is proposed to study formation of copolymers where an overall rapid polymerization can be achieved by using a suitable combination of monomers. This will enable a wider choice of polymer properties to be obtained while still obtaining rapid cure.

EXPERIMENTAL

The reactions were carried out in a Rayonet RPR-100 photochemical chamber reaction by use of 254 nm lamps. The temperature of the reactor chamber was $45 \pm 1°C$, and reaction solutions were warmed to this temperature before being placed in the reactor. The rates of polymerization were measured by refractometry at $20 \pm 1°C$, as described by Collins, Bares, and Billmeyer [12]. The extent of polymerization (P) was determined from the equation:

$$P = \frac{\overline{V}_1(n_p - n_1)}{\overline{V}_2 n_2 - \overline{V}_1 n_1 - (\overline{V}_2 - \overline{V}_1)n_p}$$

TABLE 4. Effect of Monomer

Monomer	Benzophenone (mole/ $dm^3 \times 10^2$)	Trimethylamine (mole/ $dm^3 \times 10^2$)	Conversion (%)	
			At 5 min	At 10 min
Methyl acrylate	1.57	4.70	27.0	64.0
Butyl acrylate	1.57	4.71	29.7	70.6
Methyl methacrylate	1.59	4.71	0.0	0.5
Vinyl acetate	1.56	4.69	2.3	4.8

where n_p is the measured refractive index, n_1 is the refractive index of monomer, n_2 is the refractive index of polymer, $\overline{V}_1$ is the specific volume of monomer, and $\overline{V}_2$ is the specific volume of polymer.

The presence of some of the initiators changed the refractive index of the monomer to a small extent at zero time. This difference was assumed to be constant and subtracted from each reading to obtain n_p:

$$[\text{monomer}] = 1000 \ (1 - p) \ (1 - a)/M_m [\, p\overline{V} + (1 - p) \ \overline{V}_2]$$

where a is the fraction of initiators and M_m is the molar mass of the monomer.

ACKNOWLEDGMENT

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