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Factors Affecting the Ultraviolet-Initiated Polymerization of Vinyl Monomers

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ABSTRACT

Measurements of the extent of polymerization have been made for photoinitiated polymerization reactions using consistent conditions and a common monomer, butyl acrylate. Three radiation wavelengths were used and it was found that in most cases polymerization proceeded in the order $350 > 300 > 254$ nm. From the range of photoinitiators studied it was found that those of the benzoin type, undergoing cleavage, promoted reaction faster than the benzophenone type, requiring a hydrogen abstraction mechanism. At 350 nm, those undergoing a cleavage mechanism showed reaction rates following the order of their ultraviolet absorption. A hydrogen donor such as a tertiary amine was necessary for the benzophenone-type initiators. Hydrogen donors tended to have mixed effects on polymerization produced by benzoin-type initiators. From a broad range of hydrogen donors used with benzophenone it was found that aliphatic tertiary amines were the most effective.

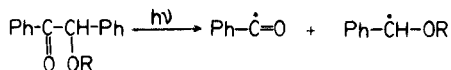
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INTRODUCTION

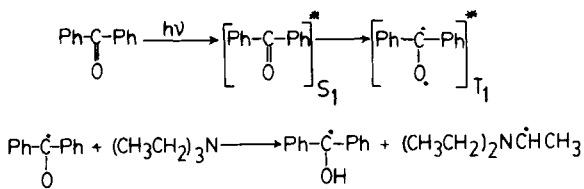
Absorption of ultraviolet radiation by photoinitiators to form active radicals is usually the result of the $n \rightarrow \pi^*$ transition of a carbonyl group. Radiation with wavelength close to this absorption maximum should produce the best results although this is often complicated by absorption of other species such as monomers.

In many comparative studies of photopolymerization systems the absorption maximum of the initiator and the wavelength of irradiation are not specified. In this work it was proposed to study polymerizations using lamps of several wavelengths and to compare the results with the absorption maxima of the photoinitiators.

Two main types of mechanism have been found to be of use in photoinitiation of polymerization. The most important mechanism is that of the benzoin-type initiators. These undergo a Norrish type 1 cleavage [1] to produce two radicals which are usually both active in initiating polymerization.



The other important class involves photoinitiated hydrogen transfer, such as that which occurs with benzophenone-type initiators.



Without a proton donor, reaction is slow or may not occur, since only the amine radical initiates polymerization; the benzophenone radical can act as a chain terminator [2]. Initial formation of a charge-transfer complex between the benzophenone and hydrogen donor may be involved [3] which is why amines have been found to be successful in this role. The photoinitiators tested in this work belong to either of the above two classes.

A series of hydrogen donors was used. These were all amines except for tetrahydrofuran. They were selected on the basis of literature reports on their utility in photoinitiation. Having the amine as part of a monomer, 4-vinylpyridine and *N,N*-dimethylaminoethyl acrylate, or part of a photoinitiator, 4,4'-bis(dimethylamino)benzophenone, were variations which were used. Previous usage of many

TABLE 1. Ultraviolet Spectral Characteristics of Photoinitiators

Photoinitiator	Absorption maxima				Extinction at lamp maxima			
	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$		ϵ_{254}	ϵ_{300}	ϵ_{350}	
	λ^a	ϵ^b	λ	ϵ				
Benzophenone	332	152	254	17,900	17,900	428	109	
Fluorenone	299	3750	257	90,300	57,300	3030	430	
4,4'-Bis(dimethylamino)benzophenone	-	-	245	16,800	13,200	9220	32,600	
N-Methylacridone	-	-	255	56,300	55,600	1500	2,000	
Benzoin	313	288	248	13,100	11,300	405	103	
Benzoin methyl ether	325	279	249	13,900	12,800	357	152	
Benzoin isopropyl ether	328	281	249	13,600	12,700	474	183	
2,2-Diethoxy-2-phenylacetophenone	337	274	253	13,100	13,000	565	229	
Benzil	325	210	259	21,000	19,300	2300	77	
Allyl bromide	-	-	-	-	168	4	3	

^aWavelength, λ , in nm.^bMolar extinction coefficient = ϵ .

TABLE 2. Percent Conversion of Butyl Acrylate by Photoinitiators

Photoinitiator	Wavelength of incident radiation (nm)					
	254		300		350	
	P ₅ ^a	P ₁₀	P _{2.5}	P ₅	P _{1.25}	P _{2.5}
Benzophenone ^b	0.0	0.0	0.0	0.0	0.0	0.0
Fluorenone	0.3	0.4	0.0	0.2	0.0	0.0
4,4'-Bis(dimethylamino)-benzophenone	1.1	2.6	0.0	0.3	0.5	1.5
N-Methylacridone	0.4	0.5	0.2	0.2	0.2	0.2
Benzoin	6.2	48.5	20.1	75.5	58.3	90.8
Benzoin methyl ether	30.1	91.7	38.4	90.2	80.7	98.0
Benzoin isopropyl ether	16.7	77.5	16.4	84.1	76.1	96.3
2,2-Diethoxy-2-phenyl-acetophenone	70.9	99.0	76.7	97.1	91.8	99.9
Benzil	0.9	2.0	0.1	0.6	0.0	0.4
Allyl bromide	0.4	0.7	0.2	0.2	0.0	0.0

^aP_X = % (mass) conversion of monomer (butyl acrylate) to polymer after X min. X = 1.25, 2.5, 5, and 10 min.

^bConcentration of photoinitiator was $(1.57 \pm 0.01) \times 10^{-2}$ mol/dm³ in each case.

of these amines by a number of workers involved different conditions or lamps and makes comparison difficult.

EXPERIMENTAL

The reactions were carried out using a Rayonet RPR-100 photochemical chamber reactor using 254, 300, or 350 nm lamps. The temperature of the reactor was $45 \pm 1^\circ\text{C}$, and reaction solutions were warmed to this temperature prior to being placed in the reactor.

Butyl acrylate was used as monomer in all reactions and no other diluent was used. The butyl acrylate was distilled under vacuum prior to use.

The degree of polymerization was measured by refractometry as described previously [4]. Data reported are from duplicate measurements. The standard deviation of all data was 1.68%, giving 90% confidence limits of $\pm 1.94\%$.

TABLE 3. Percent Conversion of Butyl Acrylate by Photoinitiators with Triethylamine

Photoinitiator	Wavelength of incident radiation (nm)					
	254		300		350	
	P ₅ ^a	P ₁₀	P _{2.5}	P ₅	P _{1.25}	P _{2.5}
Benzophenone ^b	25.0	70.3	32.0	76.0	35.8	82.0
Fluorenone	7.5	19.7	1.2	6.2	2.0	10.1
4,4'-Bis(dimethylamino)-benzophenone	0.7	2.4	0.7	1.7	0.4	1.9
N-Methylacridone	1.5	6.8	0.0	1.5	0.7	1.1
Benzoin	21.3	60.7	46.7	74.5	66.8	93.0
Benzoin methyl ether	56.9	81.5	60.9	85.7	79.6	96.7
Benzoin isopropyl ether	47.7	72.6	47.7	69.7	63.9	67.3
2,2-Diethoxy-2-phenyl-acetophenone	68.9	89.8	72.3	92.2	89.5	99.6
Benzil	18.7	41.0	8.2	19.4	10.6	21.6
Allyl bromide	0.5	0.7	0.2	0.3	0.0	0.2

^aP is as defined in Table 2.

^bConcentration of photoinitiator was $(1.57 \pm 0.01) \times 10^{-2}$ mol/dm³ and triethylamine was present at $(4.71 \pm 0.01) \times 10^{-2}$ mol/dm³ in each case in butyl acrylate.

RESULTS AND DISCUSSION

Though the major absorption maxima of the photoinitiators (Table 1) were at about 250 nm ($\pi \rightarrow \pi^*$), the absorption responsible for radical formation ($n \rightarrow \pi^*$) maximized between 299 and 337 nm. It was found that polymerization (Tables 2 and 3) proceeded most rapidly using 350 nm lamps. At 300 nm irradiation the reaction was faster than at 254 nm. The intense absorption band at about 250 nm still gave appreciable absorption at 300 nm, thereby reducing penetration of the radiation into the reaction solution. Absorption of radiation by other than the $n \rightarrow \pi^*$ transition of the photoinitiator will reduce the rate of polymerization since the amount of radiation available is constant. Both the selectivity of the wavelength and the penetration of that wavelength into the reaction solution are important considerations for achieving the maximum polymerization rate.

TABLE 4. Percent Conversion of Butyl Acrylate by Benzophenone with Hydrogen Donors

Hydrogen donor ^a	% Conversion	
	P ₅ ^b	P ₁₀
Triethylamine	25.0	70.3
Triethanolamine	35.7	82.0
N,N-Dimethylaniline	9.7	59.1
Morpholine	4.7	24.9
4-Vinylpyridine	0.0	0.2
Dimethylaminoethyl acrylate	9.4	30.9
2-Dimethylaminoethanol	24.7	77.1
2-Dimethylaminoethanol/CCl ₄	30.3	75.3
N-Methylacridone	1.0	2.0
Ethanolamine	2.0	7.8
4,4'-Bis(dimethylamino)benzophenone	5.7	19.6
Tetrahydrofuran	0.0	0.0

^a Initiator was benzophenone, $(1.57 \pm 0.01) \times 10^{-2}$ mol/dm³.
Accelerator concentration was $(4.69 \pm 0.03) \times 10^{-2}$ mol/dm³.

^b P as defined in Table 2. Wavelength of incident radiation was 254 nm.

At 350 nm irradiation the extent of polymerization is proportional to the molar absorption coefficients for compounds undergoing a benzoin cleavage mechanism (Fig. 1). At other wavelengths the trend does not occur, probably because of overlap with $\pi \rightarrow \pi^*$ absorption. Each of these compounds must have similar cleavage efficiency. Photoinitiators undergoing the hydrogen abstraction mechanism do not show such a trend. This is possibly due to differences in efficiency of intersystem crossing from S₁ to T₁ and in ability to abstract a hydrogen from the amine.

A hydrogen donor is a necessity with benzophenone-type photoinitiators. The effect of triethylamine on these photoinitiators can be assessed by comparing the data in Tables 2 and 3. The radical derived from benzophenone has been found to be only a terminating species for polymerization whereas the radical from an amine can initiate polymerization [5]. 2,2-Diethoxy-2-phenylacetophenone produces radicals which have also been shown to react with hydrogen

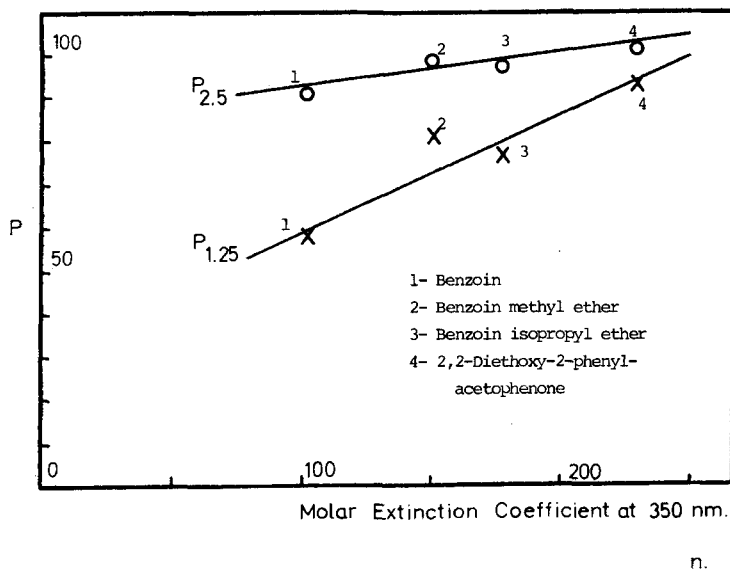


FIG. 1. Percent conversion-absorption.

donors [5]. In the current work, triethylamine produced a negligible effect on the rate of polymerization using this photoinitiator.

Allyl iodide in the presence of amines was shown to be a photoinitiator of polymerization [6]. Allyl bromide and triethylamine were tested but very little polymerization was observed in the times used for reaction in this work.

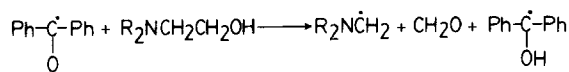
Tetrahydrofuran can also act as a hydrogen donor [7] but no polymerization was observed in the times and with the concentration used in this work. The original work [7] used tetrahydrofuran either as solvent or in 2 mol/dm³ concentration which is not suitable for most photocurable systems since the technique seeks to avoid volatile components (Table 4).

Carbon tetrachloride has previously been used in conjunction with 2-chlorothioxanthone and 2-dimethylaminoethanol to improve the cure response [8]. Carbon tetrachloride in conjunction with benzophenone and 2-dimethylaminoethanol produced no change in the percent conversion after 10 min.

The amine monomers, 4-vinylpyridine and dimethylaminoethyl acrylate, were not successful for promoting rapid polymerization. The latter provided some conversion. It was observed that the polymerizing solution in this case formed a gel, indicating that both amine initiation and acrylate double bond polymerization took place forming cross-links. This monomer should be useful for photografting reactions when included in the main polymer backbone.

N-Methylacridone was not active. This indicated that the abstraction of hydrogen from the N-methyl group, to give a resonance stabilized radical, either did not proceed or else the radical was not active in promoting polymerization. The other aromatic amine, N,N-dimethylaniline, and the cyclic amine morpholine were not as active as the tertiary aliphatic amines.

The alcoholamines, with the exception of the primary amine, ethanolamine, were more active than triethylamine. It has been proposed that the alcoholamines undergo a different mechanism of hydrogen abstraction [9].



4,4'-Bis(dimethylamino)benzophenone has been reported [1] to be a useful photoinitiator and in conjunction with benzophenone it has been said to produce enhanced photoactivity. In this work it was not found to be a successful photoinitiator at any of the wavelengths studied, and in combination with benzophenone it produced only a low percent of polymerization.

CONCLUSION

Photoinitiated polymerization using aromatic ketone initiators proceeded most rapidly at about 350 nm wavelength of irradiation. The most effective photoinitiators were found to be benzoin derivatives and in particular 2,2-diethoxy-2-phenylacetophenone. Benzophenone in the presence of tertiary aliphatic amines, especially alcoholamines, was also found to be effective. The latter does not show a decrease in surface cure rate in the presence of oxygen as do other photoinitiators [10]. Thus this property may determine the choice between a benzophenone- and a benzoin-type system.

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