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EFFECTS OF ADDITIVES ON THE LASER-INITIATED POLYMERIZATION OF 1,6-HEXANEDIOL DIACRYLATE

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ABSTRACT

Polymerization exotherms of 1,6-hexanediol diacrylate (HDDA) were generated by a pulsed laser source and recorded on a modified differential scanning calorimeter. Several aromatic carbonyl-based photoinitiators were compared with respect to maximum rate and extent of polymerization in the absence and presence of oxygen. α-Cleavage photoinitiators were more efficient than the hydrogen-abstracting benzophenone. The addition of an amine to a photocleavable initiator improved the polymerization of HDDA under an inert atmosphere, whereas triarylphosphines under similar conditions were effective in reducing the air inhibition. This synergistic effect depends on the type and structure of the additive and the photoinitiator.

The use of benzophenone in combination with an α-cleavage photoinitiator showed no significant effect upon polymerization, while extra thermal energy imposed upon the system slightly improved the polymerization.

INTRODUCTION

Molecular oxygen is known to inhibit strongly the radical-induced polymerization of vinyl monomers through the quenching of the exicted states of photoinitiators as well as the reaction with initiating radicals and growing polymer chains. This effect, commonly known as oxygen inhibition, results in a lower cure rate and, often, lower physical properties of the cured film.

One practical method for achieving a reduction in oxygen inhibition is to formulate with additives (or synergists) that can undergo rapid free-radical reactions to generate species that can scavenge oxygen molecules. Notable examples are amines, either with benzophenone or with a photocleavable initiator [1], to accelerate the cure rate in an air atmosphere.

As part of our continuing effort to study the effect of oxygen on polymerization [2, 3] and to search for methods of reducing this inhibition, we now report the effects of various photoinitiators and additives (amines and triarylphosphines) on the laser-initiated polymerization of a typical diacrylate, 1,6-hexanediol diacrylate (HDDA), both in the presence and in the absence of oxygen. The laser was operated in a multiple-pulse mode, and the exotherm data recorded on a modified DSC unit. Such equipment arrangement has been shown to be a versatile diagnostic tool in the polymerization of thin-film photocurable systems [4, 5]. The effect of temperature on the HDDA system was also investigated.

EXPERIMENTAL

The equipment arrangement for generation and detection of polymerization exotherms has been described [4]. Basically, a Lumonics 861 nitrogen laser (337.1 nm, 5 ns halfwidth flash) was directed onto a DSC exotherm unit that contained the photopolymerizable sample (Fig. 1). The DSC unit was a Perkin-Elmer DSC-1B, modified to allow irradiation of the sample through a quartz window as the sample chamber was filled with a continuous flow of nitrogen, air, or oxygen. The output of the DSC unit was fed into an Apple II Plus microcomputer with an 8-bit A/D converter. The time response of the DSC was approximately 2 s.

Samples with weights between 1.5 and 2.0 mg were used. For the experiments in this report, the laser was operated in a multiple-pulse mode. With a pulse power (p_{pulse}) of 1.0 mJ/(cm^2-pulse) and a repetition rate of 10 pulses/s, the total power falling onto the sample over a period of 100 s of irradiation was 1.0 J/cm^2.

The photopolymerizable monomer system comprised 1,6-hexanediol diacrylate (HDDA) containing a photoinitiator with or without an additive. The structures of photoinitiators and additives are given in Table 1.

HDDA (Sartomer), 2,2-diethoxyacetophenone (DEAP, Aldrich), 2-hydroxy-2-methylpropiophenone (HMP, Darocur 1173, EM Chemicals), and 2-isobutoxy-

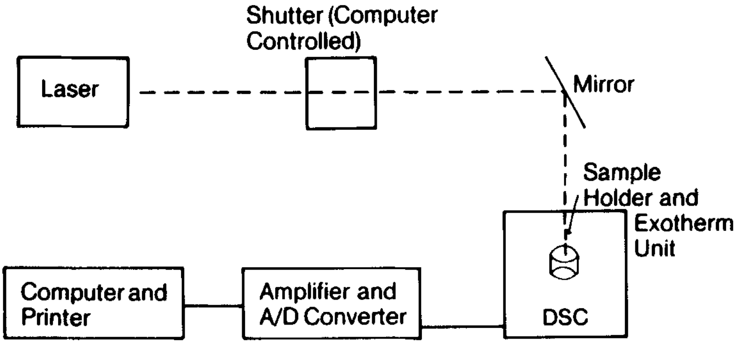


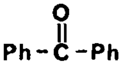
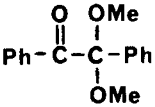
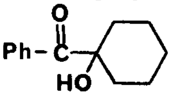
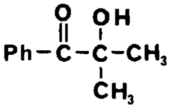
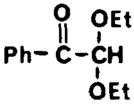
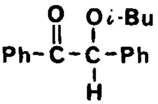
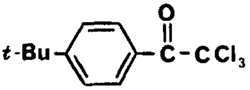
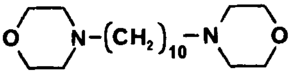
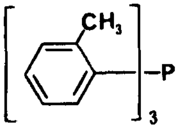
FIG. 1. Experimental arrangement for recording exotherms.

2-phenylacetophenone (IBPA, Vicure 10, Stauffer Chemicals) were distilled before use. Benzophenone (BP, Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Irgacure 651, Ciba-Geigy), and 1-benzoylcyclohexanol (BCH, Irgacure 184, Ciba-Geigy) were recrystallized twice. 2,2,2-Trichloro-*p*-*t*-butylacetophenone (TCBA, Trigonal Pl, Noury), triphenylphosphine (TPP, M&T Chemicals), and tri-*o*-tolylphosphine (T-O-TP, Lancaster Synthesis) were used as received. Triethylamine (TEA), *N,N*-dimethylbenzylamine (DMBA), and *N*-methyldiethanolamine (MDEA) were distilled. 1,10-Dimorpholinodecane (DMD) was prepared according to the literature [6] and purified further by flash chromatography on silica gel eluting with methanol-ethyl acetate (1:19).

RESULTS AND DISCUSSION

Figure 2 shows a typical exotherm recorded on the DSC exotherm unit for polymerization of a 1,6-hexanediol diacrylate (HDDA) system by the nitrogen laser. In the multiple-pulse mode, at a repetition rate of 10 pulses/s the polymerization exotherm resembles an exotherm generated by a continuous-output source. Several parameters can be directly obtained from the exotherm. H_{max}, the peak-height maximum, indicates the highest polymerization rate reached during the polymerization process and represents the overall rate of polymerization. T_{max} is the time required to reach H_{max}. The total area under the exotherm curve shows the amount of heat evolved during polymerization and is a direct measurement of the extent of polymerization. The conversion is obtained by comparison of the total heat evolved during the polym-

TABLE 1. Photoinitiators and Additives Used in the Laser-Initiated Polymerization of 1,6-Hexanediol Diacrylate

Name	Trade name	Structure	Supplier
BP	–	 $\mathrm{Ph-\overset{O}{\overset{\Vert}{C}}-Ph}$	Aldrich
DMPA	Irgacure 651	 $\mathrm{Ph-\overset{O}{\overset{\Vert}{C}}-\underset{\underset{OMe}{\vert}}{\overset{\overset{OMe}{\vert}}{C}}-Ph}$	Ciba-Geigy
BCH	Irgacure 184		Ciba-Geigy
HMP	Darocur 1173	 $\mathrm{Ph-\overset{O}{\overset{\Vert}{C}}-\underset{\underset{CH_3}{\vert}}{\overset{\overset{OH}{\vert}}{C}}-CH_3}$	EM
DEAP	DEAP	 $\mathrm{Ph-\overset{O}{\overset{\Vert}{C}}-\underset{\underset{OEt}{\vert}}{\overset{\overset{OEt}{\vert}}{CH}}}$	Aldrich
IBPA	Vicure 10	 $\mathrm{Ph-\overset{O}{\overset{\Vert}{C}}-\underset{\underset{H}{\vert}}{\overset{\overset{O\mathit{i}\text{-}Bu}{\vert}}{C}}-Ph}$	Stauffer
TCBA	Trigonal Pl		Noury
TEA	–	$\mathrm{NEt_3}$	Aldrich
DMBA	–	$\mathrm{PhCH_2NMe_2}$	Aldrich
MDEA	–	$\mathrm{MeN(CH_2CH_2OH)_2}$	Aldrich
DMD	–		[a]
TPP	–	$\mathrm{Ph_3P}$	M&T
T-O-TP	–		Lancaster Synthesis

[a] See Experimental section.

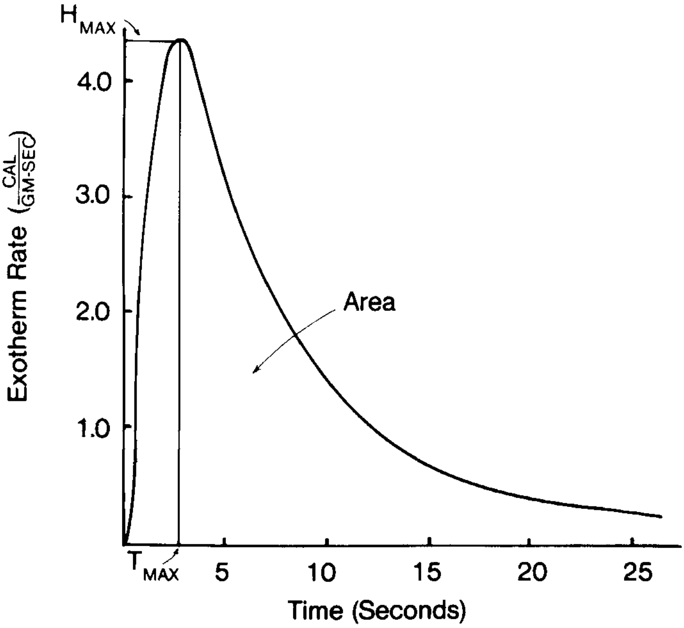


FIG. 2. Exotherm plot (DSC, 37°C) for photopolymerization of HDDA with a nitrogen laser (10 pulses/s).

erization, i.e., the area, with the total heat evolution expected for 100% conversion. For HDDA the latter value is 170 cal/g [7].

Effect of Various Photoinitiators

To determine the relative efficiency of various photoinitiators in the bulk curing of crosslinkable acrylate monomers, we carried out the laser-initiated polymerization of HDDA under various atmospheres (Table 2). The exotherm data show that benzophenone by itself is a poor initiator, particularly in the presence of oxygen. This is because the rate at which benzophenone can generate radicals by hydrogen abstraction is slow in comparison to the rate at which its triplet excited state is quenched by oxygen. When an amine such as MDEA is used as a synergist in conjunction with benzophenone, the combination has an initiating effect on the radical polymerization under nitrogen. However, this combination is less effective than photofragmenting-type initia-

TABLE 2. Exotherm Parameters for Laser-Initiated Polymerization of 1,6-Hexanediol Diacrylate (HDDA) Using Common Photoinitiators

		Exotherm parameters[b]			
Photoinitiator[a]	Atmosphere	H_{max}, cal/(g·s)	T_{max}, s	Area, cal/g	Conversion,[c] %
BP	N_2	0.9	10.4	41	24
	O_2	0.1	15.6	3	2
BP/MDEA[a]	N_2	3.7	4.1	108	64
	Air	0.8	8.1	34	20
	O_2	0.1	68	5	3
DMPA	N_2	17.6	4.4	124	73
	Air	2.3	6.3	28	16
	O_2	0.3	5.3	10	6
BCH	N_2	17.2	4.6	129	76
	Air	1.4	9.7	17	10
	O_2	0.2	9.4	11	6
HMP	Air	1.5	10.5	16	9
DEAP	Air	0.1	8.5	4	2
IBPA	Air	0.1	8.6	4	2
TCBA	Air	0.1	7.3	5	3

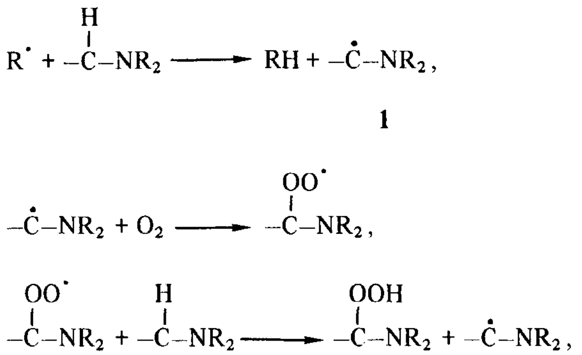
[a] 1%.

[b] Pulsed nitrogen laser operating at E_{pulse} of 1 mJ/cm^2 ; repetition rate of 10 pulses/s. DSC used to record exotherms.

[c] By comparison of the area value with the total heat evolution (170 cal/g) expected for 100% conversion [7].

tors (e.g., DMPA and BCH), as shown by the rate (H_{max}) and extent (area) of the polymerization.

When the same experiments are performed in the presence of oxygen, the polymerization of HDDA initiated either by benzophenone/MDEA or by other photoinitiators suffers severe retardation due to oxygen inhibition. Apparently, the α-aminoalkyl radical, **1**, generated from MDEA is not efficient enough in the reduction of dissolved oxygen by the following radical process:



$$R^{\bullet} + -\overset{\overset{\displaystyle H}{|}}{C}-NR_2 \longrightarrow RH + \underset{\mathbf{1}}{-\dot{C}-NR_2},$$

$$-\dot{C}-NR_2 + O_2 \longrightarrow -\overset{\overset{\displaystyle OO^{\bullet}}{|}}{C}-NR_2,$$

$$-\overset{\overset{\displaystyle OO^{\bullet}}{|}}{C}-NR_2 + -\overset{\overset{\displaystyle H}{|}}{C}-NR_2 \longrightarrow -\overset{\overset{\displaystyle OOH}{|}}{C}-NR_2 + -\dot{C}-NR_2,$$

or

$$ROO^{\bullet} + -\overset{\overset{\displaystyle H}{|}}{C}-NR_2 \longrightarrow ROOH + -\dot{C}-NR_2.$$

The results also indicate that, among photocleavable initiators employed in the polymerization of air-saturated HDDA, DMPA, HMP, and BCH are more effective than DEAP, IBPA, and TCBA.

We also investigated the effect of adding benzophenone/MDEA to HDDA already containing DMPA or BCH photoinitiator (Table 3). There is no change in the rate or extent of polymerization when the experiment is conducted in an inert atmosphere. The polymerization is still inhibited by oxygen under conditions of oxygen saturation. When the experiment is repeated in air, there appears to be a weak additive effect due to the benzophenone/MDEA initiating system, as indicated by some improvement in the H_{max} and area values.

Effect of Amine/Photoinitiator Combination

Since aliphatic amines are frequently employed as synergists with benzophenone, we measured the effect of adding an amine to HDDA containing an α-cleavage photoinitiator (DMPA and BCH, Table 4). Three kinds of amines were selected for the study: trialkylamines (TEA and DMBA), an aminoalcohol (MDEA), and an aminoether (DMD).

TABLE 3. Effect of Dual Initiator on the Laser-Initiated Polymerization of HDDA[a]

			Exotherm parameters			
Photo-initiator	Second initiator	Atmosphere	H_{max}, cal/(g·s)	T_{max}, s	Area cal/g	Conversion, %
DMPA	BP/MDEA	N_2	16.0	5.4	130	76
		Air	3.5	6.4	53	31
		O_2	0.1	10.9	5	3
BCH	BP/MDEA	N_2	13.2	5.4	123	72
		Air	3.4	7.5	35	21
		O_2	0.1	20	2	1

[a] See footnotes to Table 2.

The exotherm data in Table 4 show that addition of triethylamine (TEA) to DMPA does not significantly alter the rate and extent of polymerization under nitrogen. These results support an earlier report [8], which showed that a TEA/photoinitiator combination has no effect on the rate of acrylate polymerization carried out in an inert atmosphere.

However, the addition of other amines causes noticeable increases in the rate and, more obviously, the extent of polymerization. Within experimental error, the relative photopolymerization efficiency of the amines increases in the order: no amine $\approx$ TEA $<$ DMBA $<$ MDEA $\leqslant$ DMD. In other words, the reactivity increases in the order of trialkylamines, aminoalcohol, and aminoether. The same trend of reactivity has been observed with the UV curing, with a conventional light source, of unsaturated polyesters [9] and a clear varnish containing acrylate oligomers [6].

In a previous report [2] we showed that amines act as hydrogen donors for radicals (especially benzoyl radicals) produced by DMPA and BCH photoinitiators. It seems likely that the order of reactivity of amines observed above reflects the ease of hydrogen abstraction from amines. DMBA, for example, is a better H-donor than triethylamine, due to the easily abstracted benzylic H atoms in DMBA.

Under conditions of oxygen saturation, the rate and extent of cure are substantially lower than those under nitrogen, the rate being ~2% and the extent

TABLE 4. Effect of Amines on the Laser-Initiated Polymerization[a] of HDDA Containing an α-Cleavage Photoinitiator

Photo-initiator[b]	Amine[c]	Atmosphere	Exotherm parameters H_{max}, cal/(g·s)	T_{max}, s	Area, cal/g	Conversion, %
DMPA	–	N_2	13.0	3.9	84	49
		O_2	0.2	8.0	8	5
	TEA	N_2	13.0	4.0	91	54
		O_2	0.2	10.3	9	5
	DMBA	N_2	13.6	3.8	111	65
		O_2	0.2	12	10	6
	MDEA	N_2	17.2	4.1	125	74
		O_2	0.2	4.7	6	4
	DMD	N_2	17.5	3.7	130	76
		O_2	0.5	9.8	17	10
BCH	–	N_2	12.9	3.9	88	52
		O_2	0.2	5.5	7	4
	TEA	N_2	13.4	3.8	94	55
		O_2	0.1	15	7	4
	DMBA	N_2	13.8	3.7	119	70
		O_2	0.1	59	8	5
	MDEA	N_2	16.2	3.7	125	74
		O_2	0.2	5.3	7	4
	DMD	N_2	17.0	3.4	127	75
		O_2	0.3	7.9	13	8

[a] See footnotes to Table 2.
[b] 0.5%.
[c] 1%.

~10% of the values obtained under nitrogen (Table 4). Decker and Fizet [10] observed a sixfold decrease in the polymerization quantum efficiency when a trimethylolpropane triacrylate (TMPTA) solution is irradiated in the presence of air instead of nitrogen. They estimated that approximately 84% of the initiator radicals, mostly benzoyl radicals, are scavenged by atmospheric oxygen.

In an attempt to reduce the oxygen inhibition, amines were added as coinitiators with DMPA and BCH photoinitiators (Table 4). Exotherm data show no improvement in either the rate or extent of cure obtained when an amine was present. The failure of the amine to improve the cure rate under oxygen seems to contradict earlier reports [1]. Berner and coworkers [11], for instance, found that a combination of a photoinitiator and an amine shortens considerably the curing time of acrylate-based formulations in air. It should be noted that our experiments were carried out under an oxygen atmosphere, whereas, in practice, the polymerization of UV-curable systems is performed only under partial oxygen saturation.

Effect of Triarylphosphines

Mao and Eldred, in their 1967 study of the phosphine-initiated polymerization of acrylates, showed that the polymerization is free radical in nature [12] and the rate of tri-*o*-tolylphosphine (T-O-TP)-initiated polymerization of methyl methacrylate (MMA) is significantly higher than that of triphenylphosphine-initiated polymerization [13]. Since then, there have been a few more reports on the use of phosphines [14, 15] and phosphites [14] to overcome oxygen inhibition in photopolymerization.

In our work the oxygen scavenging efficiency of triphenylphosphine(TPP) and T-O-TP has been determined, both alone (in the case of TPP) and in combination with a photoinitiator, for the laser-induced polymerization of HDDA (Table 5). The initiators employed in this study included benzophenone and six photocleavable initiators.

Triphenylphosphine by itself does have an initiating effect on the polymerization of HDDA under nitrogen, even though it absorbs only weakly at the irradiation wavelength. The molar absorptivity of TPP in methanol at 337 nm is 2.4 $L \cdot mol^{-1} \cdot cm^{-1}$. A possible complex formation between HDDA and TPP has not been ruled out. Such weak complexes between MMA and TPP have been proposed [12]. The reactivity of TPP is comparable with that of benzophenone (see Table 2), despite the fact that benzophenone absorbs about 40 times more light at the same wavelength. When the same experiments are repeated in air or oxygen, no noticeable polymerization occurs.

TPP has been shown to undergo photooxidation rapidly to yield triphenylphosphine oxide [16]. The latter, however, shows no effect upon the polymerization process.

The addition of TPP to HDDA containing benzophenone does not significantly alter the rate and extent of cure, either under nitrogen or in air. For photoinitiators that operate through an α-cleavage mechanism, combination with TPP shows neither synergistic nor additive effects when the polymerization is conducted under nitrogen. However, a synergistic effect is observed when the same combination is used to initiate polymerization of HDDA in air, as shown by increases in both the rate and the extent of cure. The effectiveness of the combination depends on the type and structure of the photoinitiator used, with the efficiency decreasing in the order: DMPA $\geqslant$ BCH $\approx$ HMP > DEAP > IBPA. It appears that benzil dialkyl ketals (DMPA) and α-hydroxyacetophenones (BCH and HMP) are more effective than dialkoxyacetophenones (DEAP) or benzoin monoethers (IBPA). The synergistic effect of TPP with DMPA, BCH, and HMP photoinitiators was so pronounced that substantial polymerization of HDDA was observed under an oxygen atmosphere.

Under our conditions, TCBA is not an effective photoinitiator. TCBA supposedly undergoes β-cleavage to yield a Cl atom that can initiate polymerization. TCBA in combination with TPP shows no effect on HDDA polymerization in air, as is the case for benzophenone.

The effect of T-O-TP on the photopolymerization of HDDA containing a photoinitiator was also investigated. T-O-TP, is, at best, half as effective as TPP under similar conditions.

The mechanism for activation between the α-cleavage photoinitiator and the phosphine and the reduction of oxygen inhibition are not understood at this stage of research. In the photopolymerization of MMA initiated by TPP [12], the proposed mechanism involves a weak charge-transfer complex formed between the carbonyl oxygen on MMA and the phosphorus atom, resulting in the formation of a methacrylate free radical. The selective activation between a certain type of triarylphosphine and aromatic ketone observed in this work indicates that the mechanism for synergism is probably much more complex than the one shown above.

Effect of Temperature

There exists a possibility of improving the rate (and extent) of cure of HDDA at elevated temperatures, because the viscosity of the system is reduced. Furthermore, when a mixture of benzophenone and a photocleavable initiator is

TABLE 5. Effect of Triarylphosphines on the Laser-Initiated Polymerization[a] of HDDA

			Exotherm parameters			
Photoinitiator[b]	Triarylphosphine[b]	Atmosphere	H_{max}, cal/(g·s)	T_{max}, s	Area, cal/g	Conversion, %
–	TPP	N_2	1.0	25	47	28
		Air	0.1	36	1	0
BP	TPP	N_2	2.2	25	95	56
		Air	0.3	35	14	8
DMPA	TPP	N_2	16.7	4.9	134	79
		Air	9.6	5.2	74	44
	T-O-TP	N_2	16.6	5.0	124	73
		Air	3.3	5.7	25	15
DMPA + BP	TPP	N_2	16.6	5.3	125	74
		Air	8.5	5.5	70	41
BCH	TPP	N_2	18.1	4.7	126	74
		Air	7.1	5.0	58	34
	T-O-TP	N_2	18.1	4.5	127	75
		Air	3.9	5.8	27	16

BCH + BP	TPP	N_2	17.2	4.5	124	73
		Air	6.5	5.4	68	40
HMP	TPP	N_2	17.3	4.6	124	73
		Air	8.6	4.8	68	40
	T-O-TP	N_2	17.5	4.7	123	72
		Air	3.3	6.3	26	15
DEAP	TPP	N_2	16.1	5.7	125	74
		Air	4.6	7.9	53	31
	T-O-TP	N_2	15.4	5.4	122	72
		Air	1.5	11.8	18	11
IBPA	TPP	N_2	12.2	5.4	115	68
		Air	2.3	7.8	29	17
TCBA	TPP	N_2	2.4	7.1	36	21
		Air	0.1	26	2	0

[a] See Footnotes b and c to Table 2.

[b] 1%.

employed as a radical source for photopolymerization, an interaction between benzophenone and the photoinitiator may occur at high temperatures. Significant amounts of thermal energy can, in principle, be used in triplet sensitization to boost sensitizer triplet levels. Energy transfer from vibronically excited triplet levels of benzophenone to photoinitiator triplets is feasible at elevated temperatures, and this energy transfer may in turn affect the polymerization. In addition, the large amount of heat generated by UV light sources during a large-scale UV curing of organic coatings further warrants such an investigation.

Exotherm data for the laser-initiated polymerization of HDDA containing DMPA and BCH photoinitiator or a mixture of DMPA and BCH/benzophenone are given in Table 6. The polymerization was performed at 37 and 90°C under nitrogen and oxygen atmospheres. It should be noted that the weight loss of the HDDA system at high temperatures is negligible. For instance, for HDDA containing 1% DMPA, the weight loss after polymerization at 37°C was 0.25%; at 60°C, 0.95%; and at 90°C, 3.9%. The results show that for HDDA containing a single α-cleavage photoinitiator under a nitrogen atmosphere, there is some improvement in the rate and extent of polymerization at elevated temperatures. In the presence of atmospheric oxygen, the extra thermal energy imposed upon the photoactive medium is still effective in reducing the air inhibition. This effect, however, is less visible under conditions of oxygen saturation.

For HDDA containing a mixture of benzophenone/α-cleavage photoinitiator, the results show no extra synergistic effect due to benzophenone.

CONCLUSIONS

The exotherm data for multiple-pulse laser-initiated polymerization of a typical difunctional acrylate (HDDA) containing various photoinitiators and additives have been presented and discussed.

1. The efficiency of several common photoinitiators in the HDDA system was demonstrated. The benzil dialkyl ketal (DMPA) and α-hydroxyacetophenones (HMP and BCH) yielded the highest polymerization rates, as expected.
2. Under an inert atmosphere, the rate and extent of cure of HDDA containing a photocleavable initiator are improved in the presence of an amine. The reactivity of amines follows the order: aminoether ⩾ aminoalcohol > trialkylamines ⩾ no amine. The polymerization is in-

TABLE 6. Effect of Temperature on the Laser-Induced Polymerization[a] of HDDA

			Exotherm parameters			
Photoinitiator[b]	Temperature, °C	Atmosphere	H_{max}, cal/(g·s)	T_{max}, s	Area, cal/g	Conversion, %
DMPA	37	N_2	17.6	4.4	124	73
	90		19.1	4.6	141	83
	37	O_2	0.3	5.3	10	6
	90		0.4	9.7	17	10
DMPA + BP	37	N_2	16.8	5.1	127	75
	90		20.2	14	141	83
	37	O_2	0.3	6.4	13	8
	90		0.4	56	18	11
BCH	37	N_2	17.2	4.6	129	76
	90		19.2	4.8	144	85
	37	O_2	0.2	9.4	11	6
	90		0.3	22	13	8
BCH + BP	37	N_2	16.5	4.5	125	74
	90		18.9	4.8	140	82
	37	O_2	0.3	4.9	12	7
	90		0.3	45	14	8

[a] See Footnotes b and c to Table 2.

[b] 1%.

hibited by oxygen, and the addition of an amine is not effective in reducing the inhibition.

3. A synergistic effect is observed when a combination of triarylphosphine and photoinitiator is used in the HDDA polymerization performed in air. This synergism depends on the type and structure of both the photoinitiator and the phosphine. DMPA, BCH, and HMP are the most effective. Benzophenone and TCBA show no effect. Triphenylphosphine is more reactive than tri-*o*-tolylphosphine.
4. Extra thermal energy imposed upon the HDDA system slightly improves the polymerization. The addition of benzophenone to an α-cleavage photoinitiator gives no effect on polymerization.

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