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Report

THREE-DIMENSIONAL PHOTOCHEMICAL
MACHINING WITH LASERS

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

May 8, 1984

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SECOND SEMI-ANNUAL TECHNICAL REPORT

on

THREE-DIMENSIONAL PHOTOCHEMICAL
MACHINING WITH LASERS

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

May 8, 1984

Sponsored by

Advanced Research Projects Agency (DOD)
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Columbus Laboratories
505 King Avenue
Columbus, OH 43201

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May 8, 1984

Lt. Col. Harry Winsor
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Re: DARPA Contract No. F49620-82-C-0077

Dear Harry:

I am pleased to submit for your consideration the enclosed sixteen (16) copies of our Second Semi-annual Technical Report, as provided for in the subject contract. I trust this report will be satisfactory to you, and that you will agree that we are making good progress toward our goal of identifying suitable candidate materials for 3-D PCM.

The research we have performed during the past six months has concentrated on improving the properties of the photosensitizers and polymer compositions used in our studies of photochemical machining. Because of the difficulties with single-beam polymerization encountered with the derivatized porphyrin photoinitiators we synthesized last year, we have used a combined system for most of our experiments this year, with meso-tetraphenylporphyrin as photosensitizer and naphthalene sulfonyl chloride as the initiator. Our research has involved varying (a) the relative concentrations of these two species, (b) the wavelengths and intensities of light used to irradiate them, and (c) the composition of the polymer solution in which cross-linking and hardening occur.

As I mentioned at the program review meeting we had in Washington in March, we find that we are able to obtain true two-beam polymerization with some of these compositions, although we still have some residual single-beam polymerization to contend with. Our research during the coming months will be directed toward eliminating this single-beam process by the use of longer-wavelength, near-IR irradiation for beam 2, which will serve to excite the triplet but (we hope) not the ground state of the tetraphenylporphyrin sensitizer. We also plan to begin using polymer compositions that are closer to the gel point than the monomer solutions we have used to date, so as to obtain a high degree of rigidity with relatively few crosslinks.

Lt. Col. Harry Winsor

2

May 8, 1984

I hope that this report will be satisfactory to you, and that you will agree that we are making good progress toward our goal of developing a prototype polymer system for photochemical machining with lasers. Should you have any questions about our work, please feel free to call me at (614) 424-5637.

Best regards,

Bob

Robert E. Schwerzel, Ph.D.
Senior Research Scientist
Organic and Polymer
Chemistry Section

RES:1a

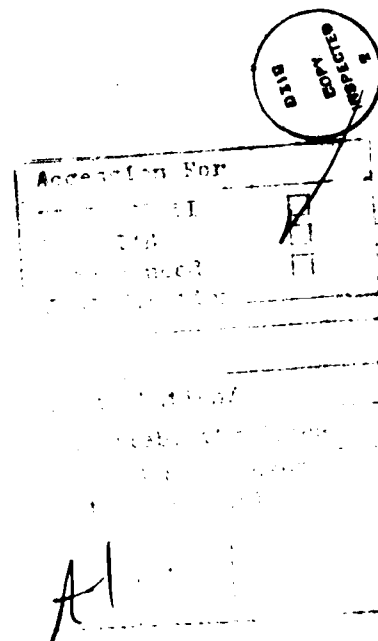
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REPORT SUMMARY

The research conducted on this project during the past six months has been successful in developing a theoretical framework for relating optical and materials properties to the performance of a PCM system, and in designing and synthesizing several novel photosensitive compounds whose spectroscopic properties make them attractive candidates for use in a PCM system. These compounds are capable, under proper experimental conditions, of initiating polymerization when they are irradiated with light beams of two different wavelengths, but not with either wavelength alone.

Battelle's early experiments were conducted with solutions of the candidate photoinitiators in liquid methyl methacrylate, for reasons of experimental convenience; the amount of polymer formed was measured by simply precipitating the resulting polymer with methanol and weighing it. While this approach worked well for screening a variety of potential photoinitiators, it is obviously unsatisfactory for the production of three-dimensional objects. Most of our work during the past six months has therefore, been conducted using monomers with added cross-linking reagents, so a solid product could be obtained directly. The research to be performed during the next six months will be directed toward the evaluation of other novel polymer compositions, containing these and other photoinitiators, that will be more capable of rapid crosslinking to provide a hard, insoluble, three-dimensional object with good surface finish and mechanical stability. This work will thus continue our progress toward the development of a viable system for performing three-dimensional photochemical machining with lasers.

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May 8, 1984

INTRODUCTION

This document represents Battelle's Second Semi-Annual Technical Report to the Air Force Office of Scientific Research on Three-Dimensional Photochemical Machining With Lasers, under Contract No. F49620-82-C-0077, for the period August 1, 1983 through January 31, 1984.

The research conducted during the past six months has been directed toward the design and development of improved photoinitiator materials, as this is a crucial requirement for the successful operation of a PCM system. After consideration of a number of possible strategies for the design of a selective two-beam photoinitiator, the strategy shown schematically in Figure 1 was adopted last year as being most likely to succeed. In this approach, a molecule is excited to its lowest excited singlet state (S_1) with photons from beam 1 having an energy below the

dissociation threshold of the molecule; it then rapidly undergoes inter-system crossing to its lowest triplet excited state (T_1). It is important that T_1 be transparent to light at the wavelength of beam 1, so no further excitation of the system can occur; in the absence of beam 2, therefore, the system will be inert, and T_1 will eventually decay harmlessly back to the ground state of the photoinitiator (S_0) with no chemical reaction taking place.

In the presence of beam 2, however, which is of a wavelength absorbed strongly by T_1 but not absorbed by the ground state, the photoinitiator will be excited to an upper triplet state, T_2 , with an energy content above the dissociation threshold for fragmentation of the molecule into reactive radicals (or ions). These species then initiate the actual polymer crosslinking process.

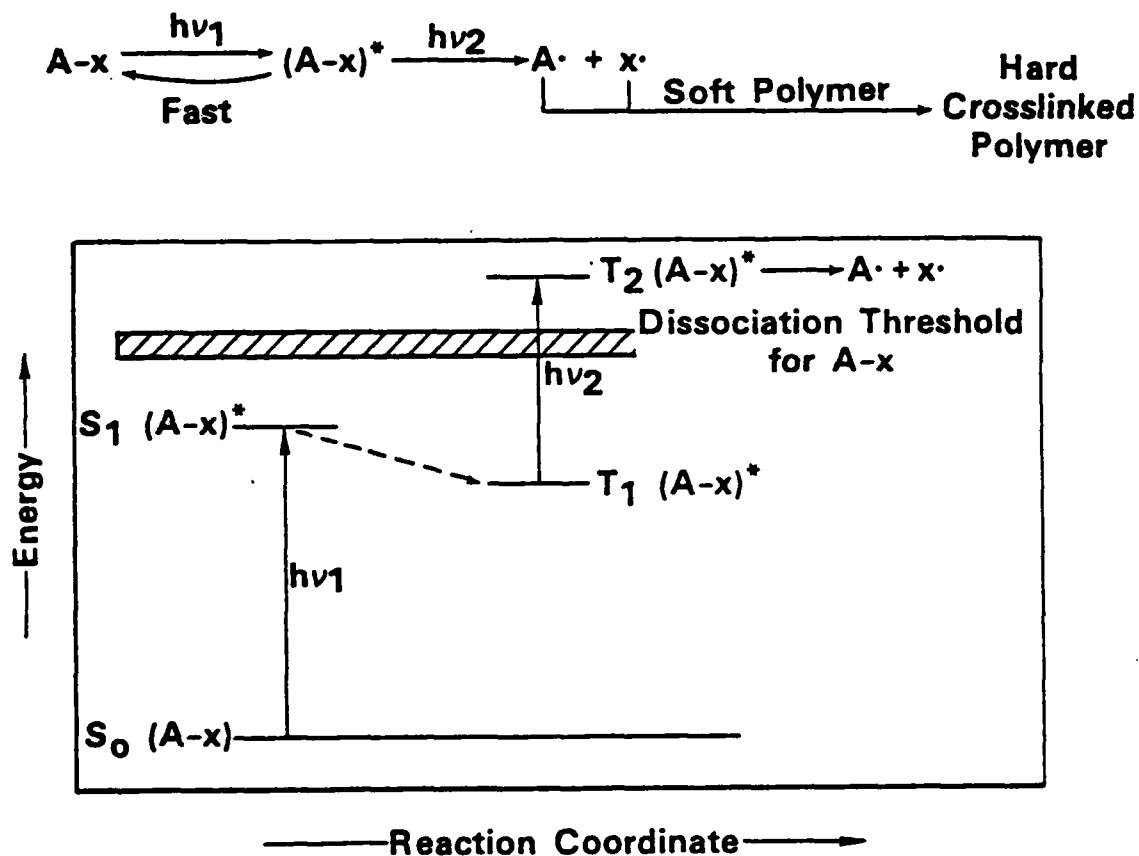
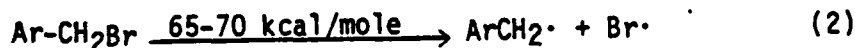
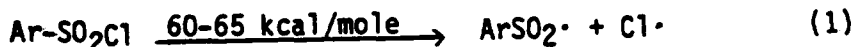


FIGURE 1. GENERAL STRATEGY FOR PHOTOINITIATOR DESIGN

More recently, we have used a similar approach in the design of triplet-sensitized reactions; in this case, a sensitizer is chosen having spectroscopic properties analogous to those shown in Figure 1, such that energy transfer from T_2 of the sensitizer to separate photoinitiator molecule will result in immediate fragmentation of the initiator.

The development of a successful photoinitiator molecule for PCM thus depends on the combination of two distinct functional groups: a light-absorbing moiety, or chromophore, with spectroscopic properties of the type just described, and a labile initiating group that can be fragmented with high efficiency once sufficient energy is delivered to the molecule.

To date, we have chosen to utilize two proven classes of initiators as our candidate materials; these are the aryl sulfonyl chlorides and the benzyl bromides, as shown generically below. There is



ample precedent for the use of these initiating groups in commercial polymerization systems; both 2-naphthalene sulfonyl chloride and 2-bromomethyl naphthalene are in widespread use. The challenge, then, has been to identify chromophoric groups (represented by "Ar" in the scheme above) which would exhibit the desired selectivity and still couple the energy of T_2 effectively into the initiator group.

As a starting point for this task, a compilation of spectroscopic data from the literature was prepared last year, as to provide a facile means of comparing the properties of compounds for which triplet-triplet absorption spectra were known. On the basis of these and other considerations (in particular, availability and/or ease of synthesis) three chromophores were chosen for initial study: these were 9,10 dibromoanthracene (an effective sensitizer from T_2 , its upper triplet

state(1); rubrene, or (5,6,11,12-tetraphenyl tetracene) (2); and protoporphyrin IX dimethyl ester,⁽³⁾ which is representative of the porphyrin family of chromophores. The structures and approximate energy levels of these systems are shown below in Figure 2. The bulk of our experimental work during the first year's effort focused on the dibromoanthracene system, because of its attractive spectroscopic properties and its widespread commercial availability. Much of our work since then has been directed toward the synthesis and evaluation of modified chromophores containing the desired initiating groups, and the evaluation of several sensitizers and photoinitiators in various monomers and polymers, particularly methyl methacrylate (MMA) and trimethylol propane triacrylate (TMPTA).

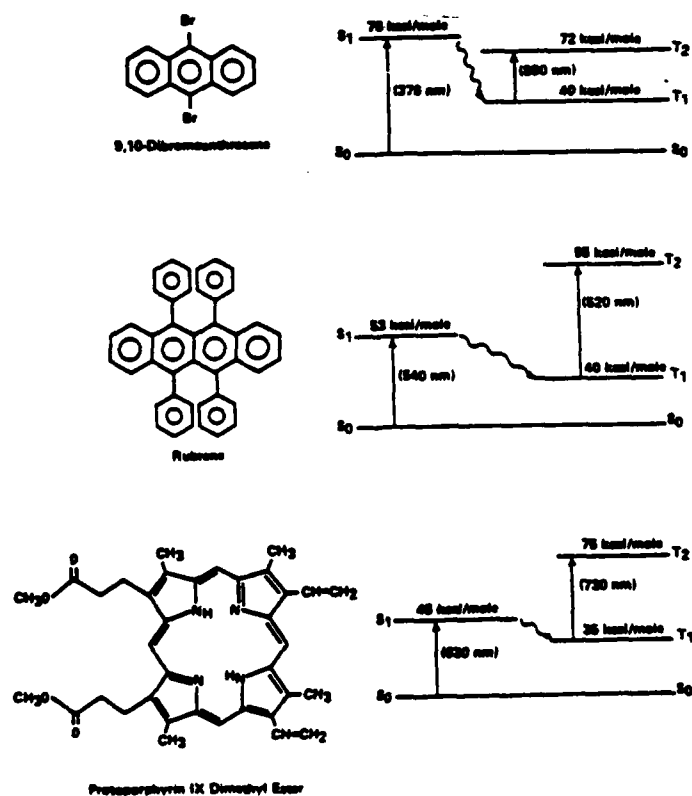


FIGURE 2. CANDIDATE PHOTOSENSITIZER MOLECULES

POLYMERIC CROSSLINKING REACTIONS

In conventional monofunctional vinyl unsaturated monomer polymerization reactions, the liquid monomer undergoes an initially slow reaction sequence to form a solid mass of material (Figure 3). About half way through the reaction sequence the monomer/polymer ratio reaches a critical value (gel point) and a rapid rise in solution viscosity is noticed along with an autoacceleration in the rate of polymerization reaction. The final stages of conversion are relatively slow in that the monomer/polymer ratio is very low and the low molecular weight monomer units must diffuse into large macroradical structures in order to terminate the polymerization process.

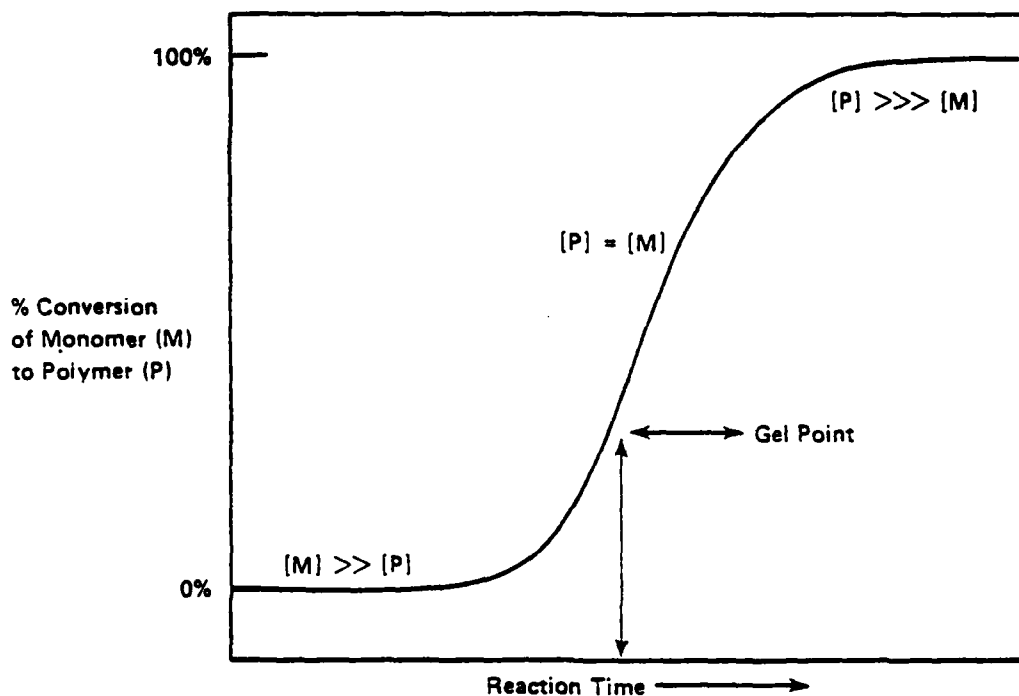


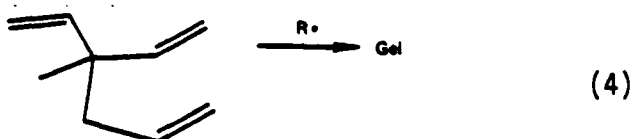
FIGURE 3. TIME SEQUENCE OF A TYPICAL VINYL POLYMERIZATION REACTION

Analysis of the overall rate equation for photoinduced polymerization reactions,

$$R_p = \frac{K [\text{monomer}][\text{photoinitiator}]^{1/2}}{k_t^{1/2}} \quad (3)$$

indicates that any substantial change in k_t (termination rate constant) strongly influences the rate of reaction. Since k_t has an indirect relationship to the monomer/polymer solution viscosity [$k_t = f(1/n)$ and $n = f(\text{monomer/polymer})$] then the percent conversion of monomer to polymer can be accelerated under certain conditions directly related to monomer or polymer concentration effects.

The most efficient method of converting a liquid reactive monomer system to a solid polymer is through the use of multi-functional vinyl unsaturated monomers that are capable of quickly developed gel or network structures at very low percentages of conversion.



The photoinduced addition polymerization of multifunctional monomers proceeds in general in three stages: formation of linear ("primary") macromolecules with pendant functional groups, branching through these groups and, finally, intermolecular crosslinking leading to gelation, i.e., the occurrence of macromolecules of "infinite" molar mass⁽⁴⁾. In addition, intramolecular cyclization reactions may occur which, in special cases, lead to cyclopolymerizations and the absence of gelation⁽⁵⁾. Differences of opinion exist as to the relative extent of the three stages, the importance of intramolecular reactions, and the applicability of the various theories to the different polymerization

stages, such as the classical statistical theories(6-8), the cascade theory(9,10), the percolation theory(11-13), and various kinetic approaches(14-15).

Simple kinetic considerations show that primary molecules are already formed at very low monomer conversions. Free radical polymerizations reach their steady-state conditions for radical concentrations of approximately 10^{-8} mol/l. If the molar mass of the primary molecules is 10^5 g/mol, and if the steady state is exclusively controlled by polymer radicals (which is approximately true for low initiator concentrations), then the steady state is reached for polymer concentrations of 10^{-3} g/l, i.e., at very low monomer conversions.

The pendant groups of primary molecules must be already subject to further reactions at these very low monomer conversions, regardless of whether all groups are equally accessible or only a fraction thereof, e.g., the groups may be attacked by primary polymer radicals (or by initiator radicals thus formed if the initiator concentration is high) and the branched alone does not lead to gelation(6), addition of polymer radicals onto primary polymer molecules and recombination of branched polymer radicals are the two ways to achieve gelation. Other termination steps, such as the disproportionation reaction of polymer radicals or the termination by initiator radicals, increase neither the degree of polymerization nor the probability for intermolecular polymer/polymer reactions. An exception may be intermolecular chain transfer to primary or branched molecules since the newly formed polymer radicals may add further monomer molecules which in turn increases the molar mass. The probability of such transfer reactions is, however, small compared to addition of polymer radicals to primary or branched molecules.

In this study, it is of prime importance to develop a unique photoinitiator system; hence, our preliminary experiments has been carried out in the well-characterized single vinyl unsaturated monomer system, methyl methacrylate.

The actual photosensitive catalyst/polymer systems studied dur-

ing this phase of the research program have involved singlet-triplet (S-T), triplet-triplet (T-T) energy transfer reactions, free radical intermediates, and unsaturated (methylmethacrylate) vinyl monomer-polymer substrates.

TWO-PHOTON LASER STUDIES

While experiments based on the use of arc lamps and filters were adequate for the initial screening of candidate photosensitizers and photoinitiators, any ultimate PCM system will almost certainly utilize lasers rather than arc lamps, to take advantage of the high energy density, precision of focus, and monochromatic radiation that lasers can provide. For this reason, our more recent experiments during the past six months have been conducted using the laser irradiation apparatus illustrated schematically in Figures 4 and 5. In these experiments, two tunable dye lasers have been used: a Phase-R flashlamp-pumped dye laser which provides beam 1, and a Molelectron nitrogen-laser pumped dye laser, which provides beam 2. These lasers provide the flexibility of being easily switched from one wavelength to another by changing the dyes utilized, and they can be synchronized to fire within a microsecond of each other to ensure that the triplet states populated by beam 1 can be "caught" by beam 2 during their brief lifetime. The sample, which is degassed and sealed under vacuum to remove oxygen which would inhibit the polymerization process, is scanned through the beams with a 3-axis, computer-controlled translation system. Using an Apple IIe computer, this system allows simple shapes to be stored on floppy disks and recalled at will to guide the motions of the sample.

While the DBA-NSC system described previously was found to give selective 2-beam photopolymerization, this system responds only to near-UV light (which is difficult to obtain from lasers with high efficiency). Therefore, a variety of other photosensitizers which respond to visible light were examined. On the base of its known photochemical properties and its spectroscopy, meso-tetraphenyl porphyrin (TPP) has been used for most of our laser irradiations to date, with naphthelene sulfonyl chloride NSC as the photoinitiator.

The spectroscopy of TPP is depicted in Figure 6, which shows both the normal (singlet-singlet) absorption spectrum and the triplet-

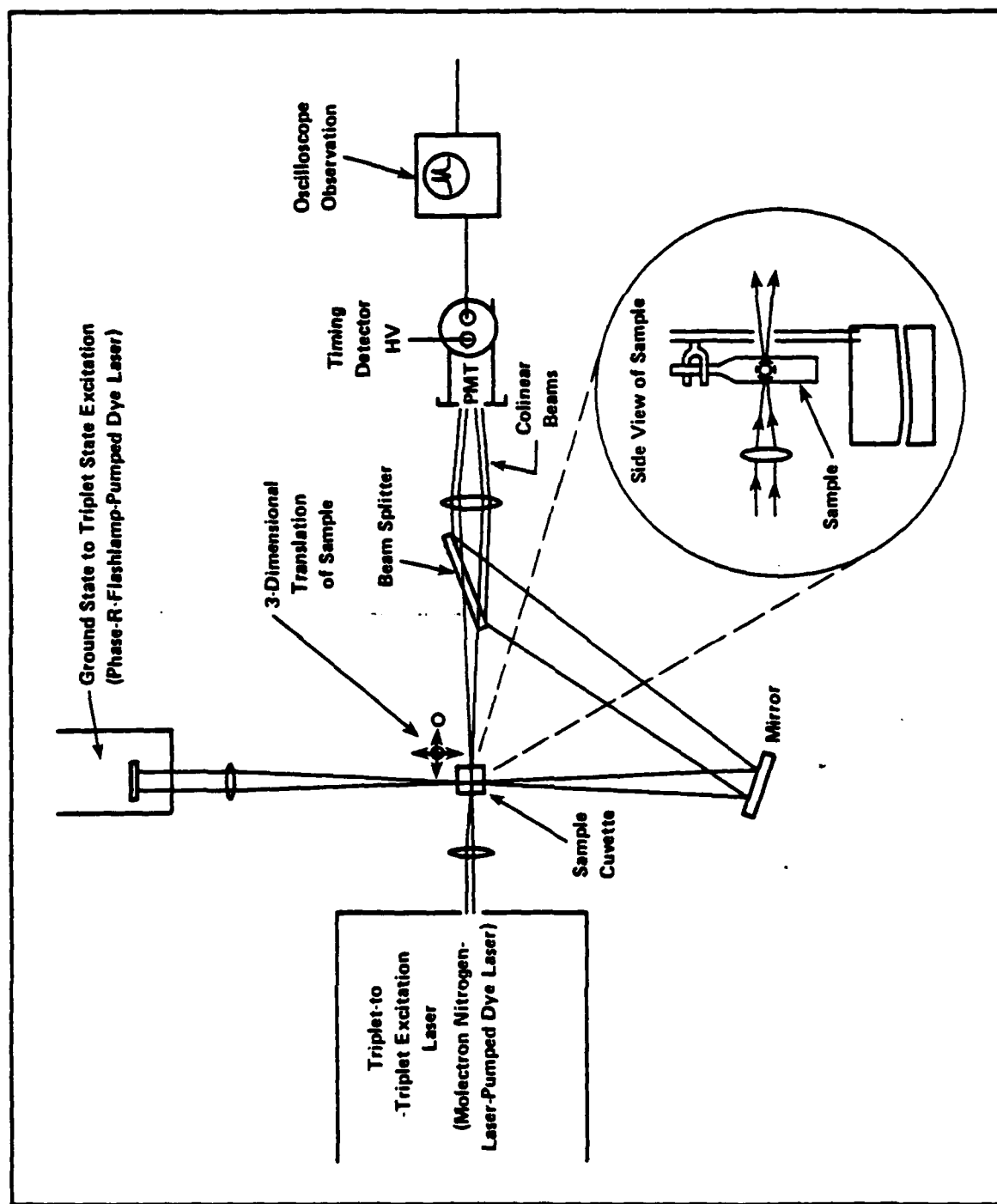


FIGURE 4. ILLUSTRATION OF TWO-BEAM LASER IRRADIATION SYSTEM

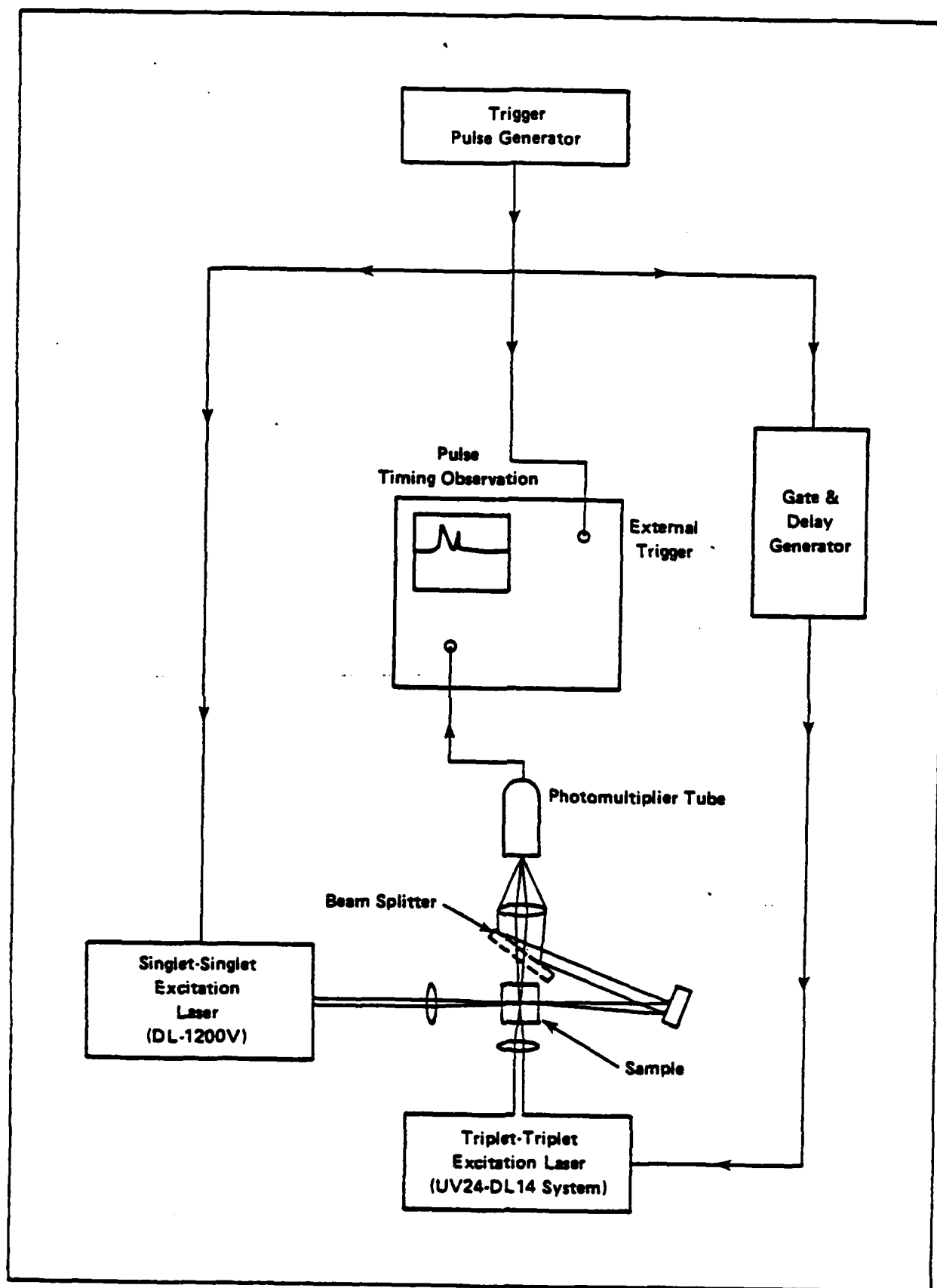


FIGURE 5. SCHEMATIC ILLUSTRATION OF LASER TRIGGERING SCHEME

triplet absorption spectrum measured by flash photolysis(16). It can be seen that there are several peaks in the 500-650 nm range which can be used to excite the molecule with beam 1; in practice, we have utilized the 600 nm peak, which matches the lasing wavelengths of rhodamine 6G in methanol. Two possibilities exist for beam 2; the wavelength range around 450 nm, where the triplet absorbs much more strongly than the singlet, and the peak at 780-790 nm, where the singlet does not absorb at all.

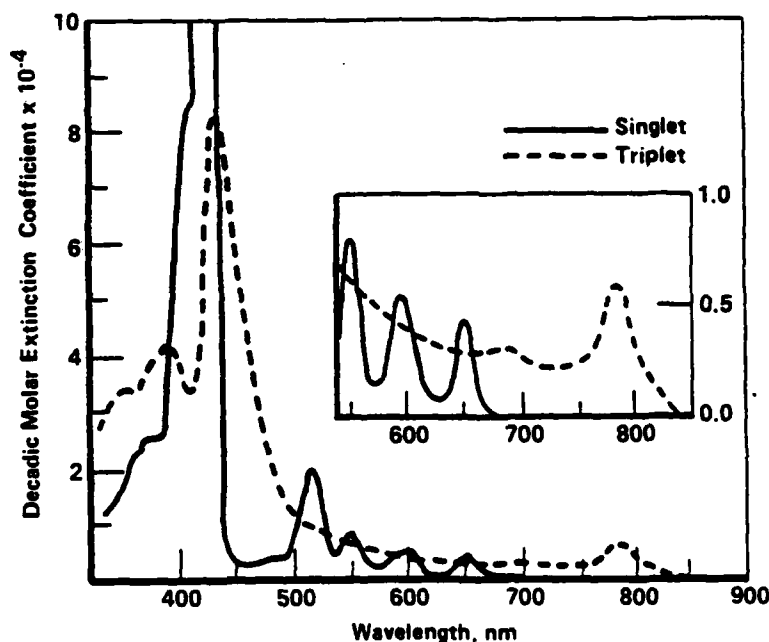


FIGURE 6. SINGLET-SINGLET AND TRIPLET-TRIPLET ABSORPTION SPECTRA FOR MESO-TETRAPHENYLPORPHYRIN.

We find that the use of 450 nm for beam 2 allows the fabrication of crude 3-dimensional shapes, although some residual single beam polymerization does occur, primarily in beam 2. Experiments using 3,3'-diethyl oxatricarbocyanine (DOTC) perchlorate as the dye for beam 2, with emission in the 750-780 nm range, have given a few examples of selective 2-beam polymerization without single-beam polymerization, but the sensitivity to date seems far lower than with the shorter wavelength; that is, the irradiation times are considerably longer to obtain a given amount of polymerization. Representative data for these laser experiments are presented in Table 1.

TABLE 1. DATA ON LASERS AND MATERIALS INTERACTIONS USED
IN TWO-PHOTON EXPERIMENTS ON POLYMERIZATION OF METHYL
METHACRYLATE WITH PORPHYRIN SENSITIZATION

	Laser 1 Phase-R DL1200V		Laser 2 Molelectron UV24-OL14	
Pulse Energy	E_1	100 mJ	E_2	0.2 mJ
Area of Beam	A_{b1}^2	$5 \times 10^{-2} \text{ cm}^2$	A_{b2}^2	$5.0 \times 10^{-3} \text{ cm}^2$
Time of Pulse	τ_1	250 ns	τ_2	8 ns
Repetition Rate (Pulses per Second)		0.33 Hz		0.33 Hz
Wavelength	λ_1	590-620 nm	λ_2	730-780 nm
Bandwidth	$\Delta\lambda_1$	$\pm 2 \text{ nm}$	$\Delta\lambda_2$	$\pm 0.1 \text{ nm}$
Effective Optical Path Length at Intersection Point	z_1	0.07 cm	z_2	0.25 cm
Estimated Absorptivity of Porphyrin Sensitizer times concentration	$(\alpha_1 C_1)$	0.2 cm^{-1} at 620 nm	$(\alpha_2 C_2)$	0.4 cm^{-1} at 730 nm

SUMMARY AND CONCLUSIONS

The research performed during the past six months has been successful in demonstrating the laboratory feasibility of crossed-beam photopolymerization. Our work has shown that it is possible to fabricate simple three-dimensional shapes using intersecting laser beams, although single-beam polymerization is still a problem. The excited-state spectroscopy of a candidate sensitizer, meso-tetraphenyl porphyrin, has been well characterized from the literature and in our laboratory, and a laser irradiation system has been designed to exploit the "windows" of selective triplet-triplet absorbance which this compound offers. Future work on this program will seek to further improve both the sensitivity and the physical properties of the polymer compositions, so as to obtain a hard, solid polymer with relatively fewer crosslinks than are required at present.

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