

Photopolymerization of Methylmethacrylate: An Inexpensive, Open-Source Approach for the Undergraduate Lab

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ABSTRACT

Light-cured polymer resins are plastics that harden after exposure to UV or visible light. The market for UV resins is expanding due to their environmental and economic benefits over conventional polymers. Using light to cure the resin allows the raw monomer to be formulated and delivered to a substrate with little to no solvents or volatile organic compounds (VOCs). Traditional industrial production of photocure products utilizes mercury vapor lamps that require a constant flow of water to prevent the light source from overheating. This research details an apparatus fabricated with open-source electronics to cure and control the polymerization process. The solid-state LED source is compact, inexpensive, customizable, and provides high-intensity (250mW/cm² per LED) irradiation that is easily directed. These features make it readily deployable in an undergraduate or research setting for small-scale experimental use. Proof of concept is demonstrated through a photoinitiator system formulated with Michler's ketone (4,4'-bis(dimethylaminobenzophenone) and benzophenone to achieve 97% conversion of methyl methacrylate into a high molecular weight resin. The effect of other photosensitizers and hydrogen donors on cure speed, molecular weight, yellowing and monomer conversion are reported for similar resins.

INTRODUCTION

Photocure polymers are a type of specialty plastic product that uses visible or ultraviolet (UV) light to cure a liquid mixture into a solid. They serve a variety of applications as adhesives and inks for the printing industry and other technology sectors such as electronics fabrication (lithography), dental fillings, coatings, paints and packaging. The economic and environmental benefits have increased interest in both academia and industry. Resins can be made to cure within seconds, allowing roll-to-roll processing at high speeds. Formulations with little or no volatile organic compounds (VOCs) produce less waste than conventional coatings. UV radiation is non-ionizing and presents no danger aside from prolonged skin and eye exposure (Yagci, Jockusch & Turro 2010).

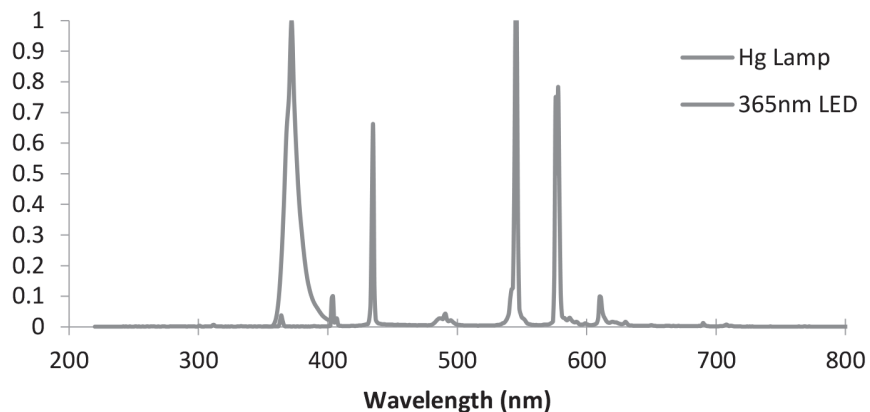
Commercial production typically utilizes mercury vapor lamps,

which provide high UV output at the cost of low energy efficiency. They produce heat and require a constant flow of water to cool them. Figure 1 shows the normalized output lines of a medium-pressure mercury vapor lamp in blue and a 365 nm light-emitting diode in red. Much of the output of the mercury lamp is lower energy, visible light that is outside of the UV region (>400 nm). Additionally, the light from gas discharge lamps propagates in all directions, necessitating shielding for safety and expensive quartz optics to direct and focus the light.

In contrast, light-emitting diodes (LEDs) provide a narrow emission band (shown as the red peak in Figure 1) and offer higher energy efficiency. As a result, the wasteful heat is reduced and can be managed through a passive heat sink, making active water-cooling unnecessary. The efficiency, however, comes at the cost of sensitivity; the lifetime of LEDs is significantly decreased if operated at a high temperature. LEDs are effectively a point source that can easily be harnessed and pointed at the target without secondary optics. Until recently, ultraviolet LEDs were costly and limited in emission and power, but this has changed and high-power (>1 W) LEDs are readily available in 365, 395 and 405 nm varieties.

FIGURE 1

Emission Spectra of UV Sources



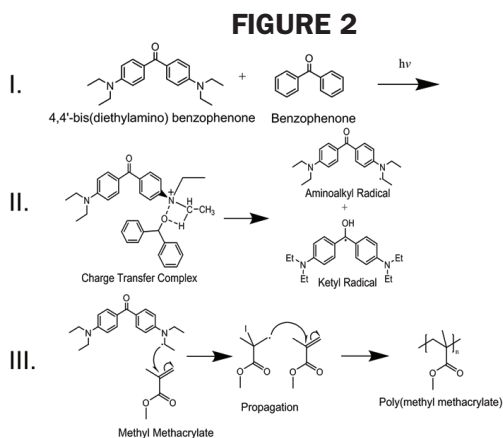
Detailed in this article is the fabrication of a UV photochemical reactor driven by an open-source microcontroller and off-the-shelf electronic components. Functionality of the reactor system is illustrated by the development of a UV-cured poly(methyl methacrylate) coating based off a class of photoinitiators called alkylaminobenzophenones.

Photoinitiator Chemistry

Photoinitiators are molecules that absorb light, that become “excited” and undergo a series of processes to transfer energy to the monomer to initiate the polymerization. Photoreactions are complex processes that can take many routes, some leading to undesirable side products that decrease efficiency and hinder chain growth as reported by McGinniss, Provder, Kuo and Gallopo (1978). The discrete emission of LEDs presents a unique problem in formulation, and initiators must be selected to match the emission of the LED.

In an ideal photopolymerization process, the excited initiator forms a radical that attacks and breaks a double bond on the monomer. Radicals are highly reactive species that are unstable, short-lived (on the order of microseconds) and sensitive to oxygen and moisture (Wamser, Hammond, Chang & Baylor, 1970).

This radical then attacks the double bond of another monomer and forms a single bond with it. The radical continues to be passed, forming single bonds between monomers, until termination or quenching occurs and the radical becomes unreactive, as shown in Figure 2.



The reaction caused by the excitation of the photoinitiator can take the form of a molecular cleavage yielding free radicals (a type I mechanism), or a hydrogen-abstraction process (a type II mechanism). Each mechanism has different advantages as explained by Green (2010), but the present work focuses on a well-established class of Type II initiators, alkylaminobenzophenones, chiefly Michler's Ketone (referred to as MK or 4,4'-bis(N,N-dimethylamino) benzophenone)) and its ethyl derivative, BDEABP. MK and BDEABP were selected as the initiators for study because they have a high absorption in the 365 nm region, although other initiators are active in

this region. The mechanisms of MK/BDEABP have been thoroughly studied elsewhere (McGinniss, 1978). Benzophenone is inexpensive and can be used in high concentrations because it is readily soluble in MMA and absorbs at 230-260 nm. Light at this wavelength is less penetrating, which provides good surface cure. The disadvantage is that its low molecular weight makes it prone to migration that produces a distinct odor (Green, 2010).

Experimental Methodology

Micheler's Ketone (MK), 4,4-bis(dimethylamino) benzophenone and its ethyl derivative, BDEABP were obtained from Fischer Scientific. 3,5-N,N-Tetramethylaniline (TMA) was purchased from TCI Corporation. Benzophenone (BP) and tris(trimethyl silyl) silane (TTMSS) was obtained from Sigma Aldrich. All chemicals were used without further purification. Polymerizations were performed in a glass scintillation vial with only monomer and photoinitiator(s) or in a solution with tetrahydrofuran (THF) or toluene. Scintillation vials were selected for the reactions because of their low cost. They are effectively single-use glassware; the polymer hardens in the container and is difficult to remove and clean even with aggressive solvents. Before reacting, the headspace in the vial was purged with N₂ then quickly sealed. To calculate the yield, a gravimetric method was employed. The unreacted, volatile components were evaporated from the vial in a furnace at 60°C under a reduced pressure of 7.6 mmHg. All yields are determined gravimetrically. A control experiment was performed by charging a vial with 10mL MMA, 4.8 % BDEABP and 4.8% BP, flushing with N₂ then leaving the capped vial on a lab bench under ambient conditions for 2 months. Gel-permeation chromatography (GPC) samples were prepared at a concentration of 10 mg/mL of dried product dissolved in THF. A Waters GPC fitted with a Styragel column was used for the analysis and calibrated with polystyrene standards. The light intensity at 365 nm was calibrated using a G&R labs Model 202 UV intensity meter and a distance scale marked on a ring stand.

Electronics and Fabrication

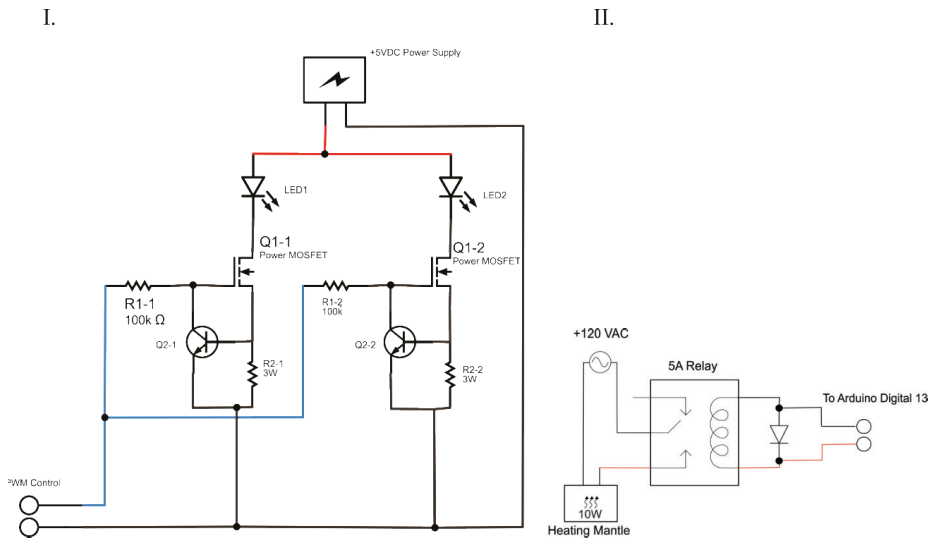
The Arduino microcontroller serves as the platform for the radiation source, and was chosen because of its flexibility, ease of programming, and customizability. The ultraviolet source was designed using commercially available 3 Watt 365 nm UV LEDs and heat sinks (Mouser Electronics) powered by a 5Volt/5Amp supply (TDK Lambda).

A circuit to interface LEDs to a power supply to microcontroller is presented in Figure 3-I. The signal from the microcontroller is amplified by a small general-purpose NPN transistor, which activates an N-channel FET that

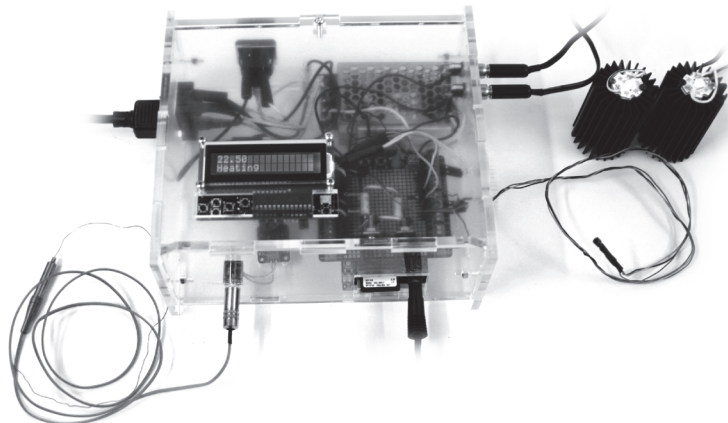
can switch the 700 mA load of the LED. Two of these circuits in parallel were assembled on a proto-shield from Sparkfun Electronics. Screw terminals on the proto-shield facilitate simple reconfiguration.

A heating control for a 120 Volt AC heating device was fabricated using a low-power coil Omron 5 V relay rated for switching 5 A at 120 VAC. As shown in Figure 3-II, the relay is connected to a pass-through outlet, so any heating or cooling device up to 500 W can be used in this configuration. A freewheeling diode is placed across the relay to dissipate power from the coil after switching and prevent it from damaging the microcontroller. A prefabricated thermocouple board with a built-in MAX 31855 amplifier chip is used to monitor the temperature, and can be called at any point in the program.

FIGURE 3



A 16x2 character LCD from Adafruit is the basis for the user interface, and provides a directional keypad in addition to the multi-color backlit display. The LCD shield uses the i2c (inter-integrated circuit) protocol for communication, which reduces the amount of pins required to control the LCD and RGB backlight from 9 and also adds a directional keypad and select button. The electronics were housed in a laser-cut acrylic enclosure using the UW-Stout FABLAB's Epilog Fusion laser.

IMAGE 1**Programming**

The program was written using the Arduino IDE (Arduino, n.d.). Add-ons called libraries are used in the program using the `#include`. The program has three main parts: `setup`, `loop`, and `end`. The `setup` initializes variables such as pin assignments. The `loop` is the heart of the program and contains the commands to control heating, irradiation time, and intensity. Within the main loop, LEDs are controlled with a pulse width modulation (PWM) signal generated by the `analogWrite` function. A value from 0-255 controls the duty cycle of the LED.

An AC heating device (such as a hotplate) can be controlled using a pass-through circuit connected to a relay. A simple `if..else` statement is used to control the temperature, which compares the set temperature to an average of 10 samples. The Arduino is also capable of more advanced options such as proportional-integral-differential (PID) control if precision temperature control is required. Adjustment of the temperature set point and duty cycle of the light source is accomplished by using the buttons on the LCD shield in an `if` statement with conditions that limit the values appropriately. The new value is then briefly displayed on the LCD before returning to the main loop. A timer to turn the LEDs on and off is incorporated by using a timer library, a long variable that runs a "done" loop after the set time has elapsed, which simply turns off the light source and relay.

The Adafruit data-logging shield contains an SD card slot and real time clock, which can log data in real time (opposed to relative time stored in the Arduino) to a file that can be processed later in any spreadsheet program.

RESULTS

Initial experiments were performed using styrene, which showed almost no reactivity to the initiator, so MMA was chosen for the study. Similar experiments (Green, McGinniss) confirm the current initiator system is not reactive with styrene or monomers with a low energy ground state and yields were very low (<15%) for styrene. Detailed results not included for this reason.

Experimentally determining the most efficient combination and relative proportions of initiators for polymerization of MMA was the main objective of this study, which was obtained by starting at relatively high (5% wt) amounts working down and increasing the ratio of benzophenone to Michler's Ketone/BDEABP dissolved in MMA. Concentrations of 0.16-5.00% weight initiator and 0.58-5.05% benzophenone were used, and the best properties (i.e. low total mass and high yield) were achieved at relatively small amounts of initiator: 0.3 weight % BDEABP to 1.88 weight %BP, approximately a 1:6 ratio. Results are shown in Table 1. The control sample that was allowed to react under ambient conditions with no high-intensity irradiation for two months yielded 67.3% conversion. In addition, the experimental source was compared to a commercial medium-pressure mercury (Hg) vapor lamp (Ace Glass Co.). Compared to the LEDs, the measured intensity of the vapor lamp was less than a single LED lamp at 365 nm. To ascertain the effect of decreased intensity and the presence of other wavelengths of light provided by the Hg vapor lamp on the polymerization, two samples were prepared with the same composition, one irradiated by the Hg vapor lamp and the other by the LEDs for 1 hour. The LED irradiated sample yielded 96% conversion compared to 88% for the Hg vapor illuminated sample, as shown in bottom rows of Table 1.

TABLE 1

Initiator Ratio (BDEABP:BP)	Weight % BDEABP	Weight % BP	Total Weight % Initiator	% Conversion
4:1	4.04	1.01	5.05	52.3
2:1	4.1	4.5	8.6	10.1
1:1	4.45	4.49	8.94	95.0
1:1	4.69	4.71	9.4	12.5
1:2	1.04	2.06	3.1	27.2
1:3	0.3	1.88	2.18	96.5
1:1 (Control, No UV)	4.81	4.81	9.62	67.3
1:1 (LED Control)	2.53	2.53	5.06	95.8
1:1(Hg Vapor Control)	2.53	2.53	5.06	87.7

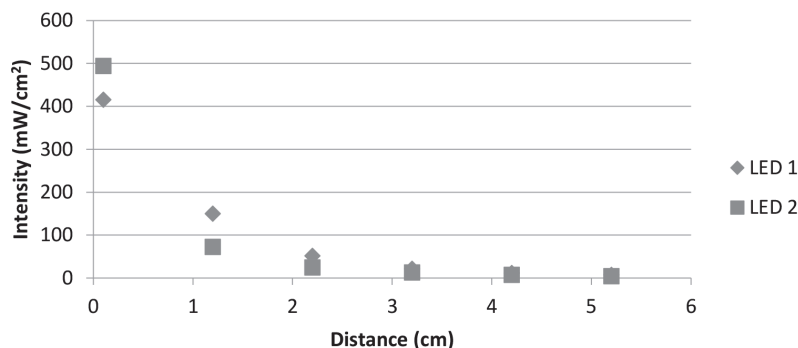
The viscosity of the samples varied dramatically with the percent conversion, as expected. Samples with low conversion were water-like, while the samples that went to near completion were difficult to remove from the

vial. After irradiation, it was observed that some of the reaction mixtures still remained water-like. After sitting overnight (without exposure to air), additional polymerization could occur and the mixture would "set" and form a highly viscous gel. The mechanism of this "living" phenomena is elusive, and a proper treatment is beyond the scope of this work. The optimal irradiation time for polymerization was determined by varying the irradiation time (from 15 minutes to 13 hours) and visually monitoring the reactor. Decomposition of the initiator occurs within minutes of irradiation. The reaction mixture changes from colorless to bright yellow quickly, long before a change in viscosity is noticeable. From these observations, it was determined that a 1 hour irradiation period is sufficient to break down the initiator. The high molar absorption of MK/BDEABP leads to yellowing even in low concentrations. Because the absorption is very high, yellowing could not directly measured and correlated with radical yield or conversion.

The measured intensity as shown in Figure 4 was 415 mW/cm² and 494 mW/cm² for the individual LEDs at 1mm from the source, which decays exponentially as the distance increases.

FIGURE 4

Intensity vs. Distance



Obtaining a high molecular weight polymer is often difficult with photoinitiated systems, as reported by McGinniss et al. (1978). Generally many radicals result in short polymer chains due to radical termination by combination. The addition of benzophenone was found to significantly decrease the molecular weight of the polymer. Raw chromatograms presented in Figure 5 and summary data in Table 2 show this trend. For the polymer produced without benzophenone, a bimodal distribution was observed, possibly due to competing mechanisms of radical formation or chain growth.

FIGURE 5

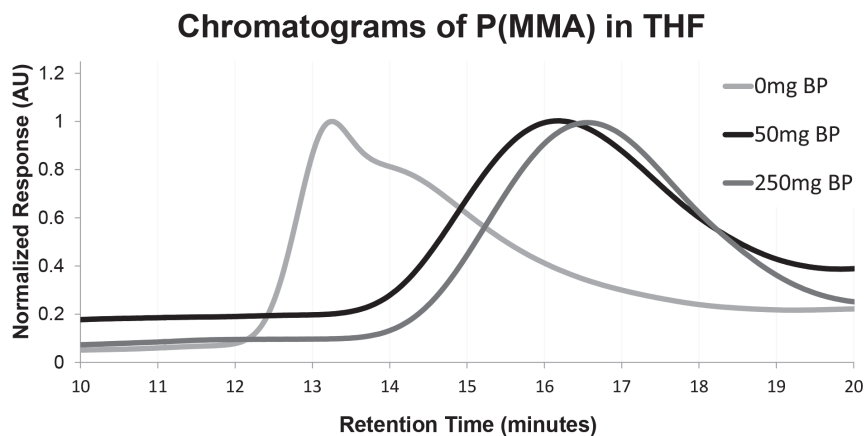
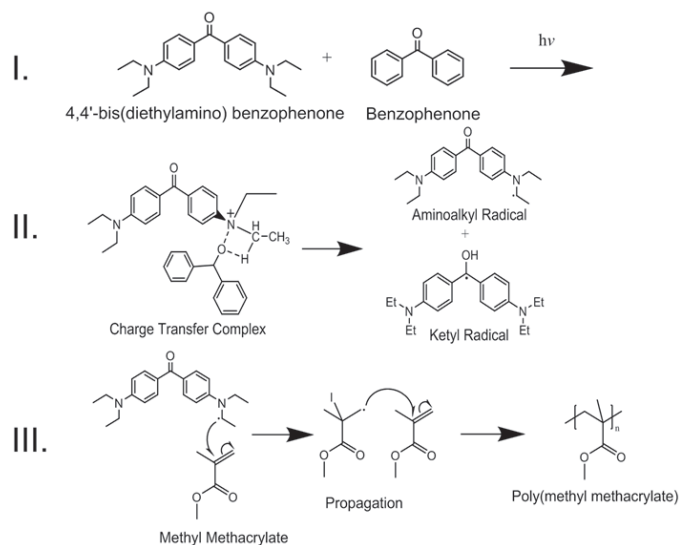
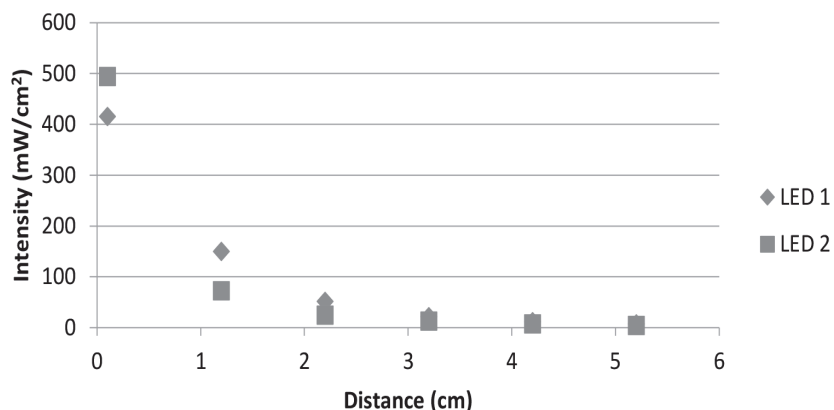


TABLE 2



Polymerizations were also attempted in two different types of solvents, THF (which is polar) and toluene (non-polar). The mixture of 50 % (v/v) solvent and monomer assumes that initiator volume is negligible. All components were readily miscible. The initiator loadings of these experiments are summarized in Table 3 (p.139) for THF and Table 4 for toluene, respectively. Neither THF nor toluene improved the yield compared to the control experiment.

TABLE 4
Intensity vs. Distance



However, once dried, the high-yield polymers produced without solvent exhibit high resistance to THF and Toluene. After addition of solvent, the solution remained biphasic for several days. These properties and GPC data confirm that the polymer has a high molecular weight, which varies significantly from MK/BDEABP acrylate systems studied elsewhere. Oxygen gas in the atmosphere causes quenching of radicals, thereby decreasing the yield. This effect was proven by performing an experiment with the vial open to the atmosphere and comparing with a control flushed with nitrogen. The formation of dark amber byproducts was observed in the vial open to the atmosphere, and the reaction mixture remained water-like in viscosity, indicating a low yield. A study performed by Lalevee et al. (2008) reports that the addition of TTMSS increases yield under air and impart hydrophobic properties to the resulting polymer, but these effects were not observed and the yield was still very low. Tetramethylaniline has also been reported by Schroeder, Asmussen, Cook and Vallo (2011) as an effective hydrogen donor, but did not significantly affect the yield even in amounts up to 1 wt%.

DISCUSSION

Despite the immediate yellowing, some samples did not reach maximum completion immediately after irradiation. Instead, the reaction mixture hardened overnight when the vial was left capped. This suggests that the polymerization may be "living," meaning that polymerization continues even though no new radicals are being formed. The full mechanism behind this phenomenon is not fully understood, but would explain the high molecular weight obtained. Conversion appears to be linear with time of irradiation. As

reported by Schroeder et al (2011), the rate of photolysis is independent of molecular mobility in a highly viscous or gelled medium. This effect contributes to the rate of initiation and may not hold true for the rate of polymerization, and the most probable explanation for the observed kinetics is that radicals and monomers are physically separated by the highly viscous reaction medium. Thus, the rate of the polymerization is effectively limited by the diffusion of radicals/monomer through the mixture. Benzophenone functions as an excellent sensitizer, and drastically increases the efficiency of both MK and BDEABP. Benzophenone is widely used in perfumery, but its low molecular weight makes it prone to migrate from the polymer matrix, since it is not incorporated directly onto the polymer chain (Green, 2010). This means that even after curing, a recognizable odor is present. Due to the aforementioned reasons, Type II systems with Michler's ketone are becoming less popular in industrial formulations, due to suspected carcinogenicity and the development of better photoinitiators. It has a high molar absorption coefficient (McGinniss et al., 1978) that results in yellowing and screening effect even in concentrations as low as 0.16% by weight. Since the triplet lifetime of the initiator is relatively long, quenching is more likely to occur than in type I systems (Green, 2010). For this reason, type II systems are inherently harder to formulate effectively. In a typical industrial coating application, raw monomers are rarely used to formulate coatings due to their volatility. Rather, oligomeric or "pre-polymerized" mixtures are delivered then fully cured with a photoinitiator. However, this study shows that raw monomer is able to be polymerized in bulk or with some solvent to make a fully-cured high molecular weight polymer.

The cost of the photocure system built in this study is much lower than commercial systems. The commercial reactor used in this study costs approximately \$1,200, while all of the components of the fabricated reactor totaled less than \$400. The Arduino and other open-source microcontrollers are an attractive option for deployment in undergraduate research settings, due to the cost and customizability. For students, they provide an insight into the fundamental aspects of instrumentation in the chemistry lab and an opportunity to design, build, and optimize a system.

CONCLUSION

An apparatus for photopolymerization studies was fabricated using an open-source Arduino microcontroller and off-the-shelf electronics. The solid-state LED source is compact, inexpensive, customizable, and provides high-intensity (250 mW/cm² per LED) irradiation that is easily directed. Photocure methyl methacrylate resins were formulated with Michler's Ketone and its ethyl derivative, BDEABP, then polymerized in bulk or solution. The effectiveness of MK/BDEABP can be improved by addition of benzophenone, a low-cost ketone. Various concentrations and proportions of initiators were used and the most effective concentration was determined to be 1:6 ratio of BDEABP to BP, which when combined composed 2 weight% of the reactants and yielded 96.5% conversion. Percent conversion was higher than reported in similar studies published elsewhere. The molecular weight of the polymer was determined using gel-permeation chromatography. Molecular weight was also found to significantly decrease with the addition of benzophenone. The cure speed and yellowing are significant drawbacks to the present system. Furthermore, exposure to oxygen significantly reduces yield and increases undesirable byproducts. Nonetheless, the feasibility of attaining a high-yield, high-molecular weight resin was demonstrated with bulk polymerization from raw monomer in a low-cost system that is easily deployable in an undergraduate setting.

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