

Effect of Thickness, Exposure Time, Photoinitiator Level, and UV Irradiance on the Kinetic and Thermodynamic Properties of UV-Curable Formulations

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ABSTRACT

In the course of investigating the effects of various composition and process parameters on the relative reactivity of ultraviolet (UV)-polymerizable formulations, differential photocalorimetric (DPC) methods were utilized in this laboratory. A two-level factorial screening experiment was conducted to determine the effects of sample thickness (mass), exposure time, UV irradiance (“intensity”), and photoinitiator level on the relative reactivity and reaction thermodynamics of UV-polymerizable formulations. The results of this study give an indication of the variability of DPC methodology and are consistent with current understandings of the kinetics of the photopolymerization process. This report also provides a detailed discussion of the use of two-level factorial design methodology in UV polymerization research activities.

INTRODUCTION

The technique of differential photocalorimetry (DPC) has been available since the 1970s^{1,2}. However, many working in the UV-polymerization field are still unaware of the value of this technology. DPC techniques can provide a great deal of important experimental information concerning the kinetics and thermodynamics of UV-polymerization and crosslinking reactions. Of course, kinetic and thermodynamic information about UV-polymerizable systems, while being of significant scientific value, also relates directly to the commercially important issues of “line speed” and “productivity”. Thus, having the ability to accurately collect this type of data is important for anyone concerned with photopolymerization chemistry and technology.

With DPC instrumentation, one can measure the relative reactivity of various formulations for comparison purposes. During a DPC experiment, a heat flow (exotherm) vs. time curve is generated that shows the rate at which thermal energy is evolved from the system during polymerization. An example of such a curve is shown in **Figure 1**. From such curves, the relative reactivity of a formulation can be determined by evaluating parameters such as the *induction time* and the time to the exotherm peak maximum (*peak max time*). The height of the curve at the peak maximum time (*peak height*) can also be used to determine relative reactivity of the system since at this point in time, the system is experiencing its maximum rate of reaction.

Induction time is the measured time interval between when the lamp’s shutter is opened to expose the sample to UV light and when the reaction actually begins to occur as evidenced by a sharp increase in the slope of the exotherm curve. (The slope of the curve at any particular time is a measure of the instantaneous acceleration of the reaction in units of mJ/s^2 .) The

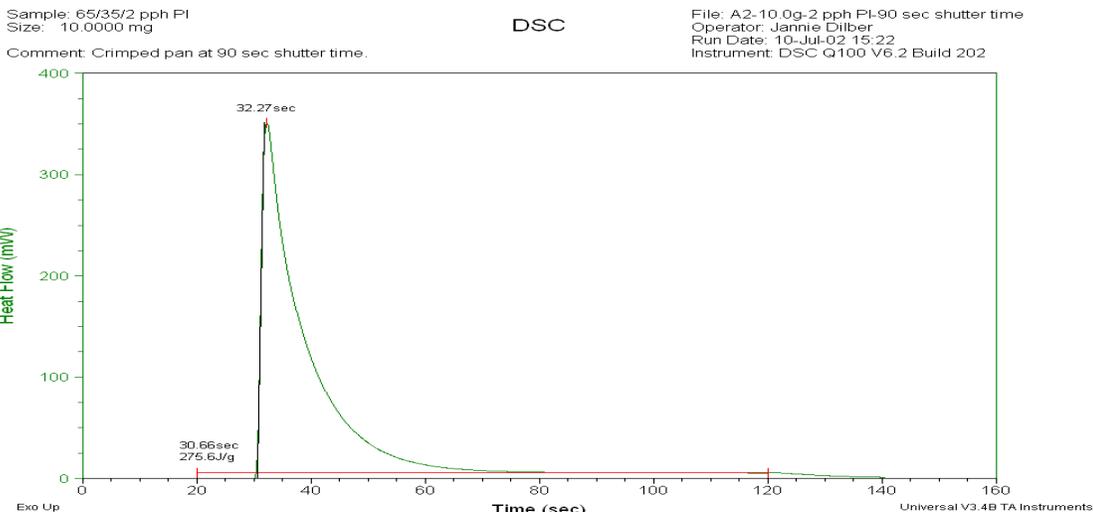


Figure 1
Sample DPC Scan with Analysis

induction time reflects the amount of inhibition that the system must overcome before actually beginning to polymerize and crosslink. It is strongly affected by the presence of inhibitors in the raw materials of the formulation, by the presence or absence of air during the reaction, by the intensity – more accurately known as the “peak power density” or “irradiance” - of the impinging UV light, and by the relative reactivity of the functional components. Thus, the induction time gives a good indication of the overall inhibiting effects of these parameters.

For this investigation, the peak max time was defined as the amount of time required for the reacting system to reach its highest rate of energy output after the induction period; the amount of time measured from when the polymerization actually starts until the exotherm curve reaches its maximum height. These data have been interpreted for this study as one of two relative measures of the overall average rate of the reaction. The peak max time is affected by the relative reactivity of the monomers and oligomers, the amount of shutter time used, and by the UV irradiance. It is reasonable to assume that a formulation exhibiting a relatively short peak max time has an overall reactivity that is higher than that of a formulation requiring a longer time to reach the maximum in the exotherm curve.

The third kinetic parameter evaluated in this investigation was the peak height. Since the height at the peak maximum of the exotherm curve represents the point in the polymerization when the reaction rate is at its maximum, its measurement gives a good indication of the relative reactivity of a given UV-polymerizable system. Systems with higher peak heights should normally have higher overall average reaction rates.

In addition to these kinetic parameters, DPC scans allow for the determination of thermodynamic data in the form of the total exotherm; the total amount of energy evolved during the polymerization reaction. This energy is primarily produced by the exothermic reactions that change acrylate functionalities (double bonds) into crosslinked polymers. Thus, the total exotherm gives a relative indication of the percent of double bonds converted to polymer. The total exotherm is often normalized with respect to the mass of the sample, as it is in the scan

shown in **Figure 1**, and recorded in joules per gram (J/g). However, in this presentation, the total exotherm is reported directly in energy units (joules). The total energy is measured by integrating the area under the curve between selected time limits. Normally, the integration is done over the time that the shutter for the lamp is actually open (*shutter time*).

Clearly, then, when utilized properly, DPC methodology provides the opportunity for research and development personnel to increase their understanding of the kinetic and thermodynamic properties of photopolymerizing systems and to make relative comparisons of these properties among different formulations. It also allows them to evaluate the effects on these properties of varying key process parameters such as the total UV energy density and the UV irradiance, while using very small samples (on the order of 0.20 to 0.50 mg) and relatively short time frames (typically <2 minutes).

As with any other instrumental method, it is important that the effects of experimental parameters be understood if reliable and reproducible data are to be obtained. The instrumental parameters of concern in this study were the *shutter time* and *UV irradiance*, while the formulation parameters of interest were the *photoinitiator level* and sample *mass* (thickness). A 2⁴-factorial designed experiment was utilized. The most beneficial element of this type of screening design is that it minimizes the total number of experiments required to evaluate the effects of many different parameters at the same time³. It also allows an estimate of standard errors to be calculated without having to evaluate large numbers of replicates⁴. The purpose of this investigation, then, was to evaluate the effects of these four independent variables on the kinetic and thermodynamic properties of UV-polymerizable model formulations using DPC techniques and a factorial experimental design.

EXPERIMENTAL

Materials:

The following raw materials were provided by their respective suppliers and were used without further purification:

ALU-350 acrylated aliphatic urethane oligomer was provided by Echo Resins and Laboratory, Versailles, MO.

Trimethylolpropane triacrylate (TMPTA), *1,6-hexanediol diacrylate (HDODA)*, and *isobornyl acrylate (IBOA)* were all provided by Surface Specialties UCB, Smyrna, GA.

1-hydroxycyclohexylphenyl ketone (Irgacure[®]184) photoinitiator was provided by Ciba Specialty Chemicals Corporation, Tarrytown, NY.

Equipment:

Denver Instrument Company, Model A-250, Analytical Balance was used to measure the mass of samples to the nearest 0.1 mg.

TA Instruments, Model Q100™ Differential Scanning Calorimeter (DSC) with photo-calorimeter accessory (PCA) was used to determine kinetic and thermodynamic data for two different model formulations prepared for this study. Both the reference and sample light guides of the PCA unit (the DPC) contained 1% neutral density filters in order to reduce the emerging light intensity to approximately 30-65 mW/cm².

TA Instruments Universal Analysis software was used to analyze the exotherm curves produced during the DPC experiments. The total exotherms were evaluated through integration using the extrapolation method.

Procedures:

Preparation of formulations - A couple of different formulations were prepared and evaluated during this project. Both contained 48.75 g of the acrylated aliphatic urethane oligomer and 26.25 g of a TMPTA/IBOA/HDODA monomer blend. The three monomers were combined in a 1:1:1 ratio by mass. The only difference between the two formulations was in the amount of photoinitiator added to each.

Samples of the urethane oligomer used in this study were placed in two 4-oz dark brown glass jars. Equal masses of the three monomers were then added to each jar and these 65%/35% by mass oligomer/monomer blends were heated in an oven between 45 and 50°C to aid the mixing process. When the blends were completely homogeneous, 0.50 parts per hundred (pph) photoinitiator was added to one jar and 2.0 pph were added to the second jar. These were mixed further at room temperature until they were completely homogeneous by appearance.

DPC Methodology – Samples of the model formulations were weighed into the lids of small “hermetic” DSC pans using the analytical balance. The lids were chosen because their flat surface allows for more intimate contact with the sample cell pedestal in the DPC instrument. When weighing samples, care was taken to insure that each sample covered the same amount of surface area in the lid. The reason for this was to insure that as the mass changed, the sample thickness changed proportionally. The lids w/sample were placed on the sample pedestal and empty hermetic lids were placed on the reference pedestal within the sample cell of the instrument. The sample and reference light guides (previously adjusted to the same intensity readout) were then put in place above the sample and reference lids. The sample cell was flushed continually with air at a flow rate of 50 mL/min, allowing the polymerization reactions to be run in the presence of air to simulate what is typically done in industrial applications. The *Universal Analysis* software was then programmed with appropriate experimental parameters, the samples were polymerized, and the exotherms of the various reactions were recorded and analyzed.

Experimental Design:

Two-level factorial experimental designs involve the selection of a “high” (+) and a “low” (-) value for each independent variable to be evaluated⁵. Since this study involved four independent variables, a 2⁴-factorial design was developed and a total of four high and four

low values were selected. As indicated previously, the low and high values for the photoinitiator level were 0.50 pph and 2.0 pph, respectively.

For mass, the high value selected was 4.0 mg and the low value was 2.0 mg. These values were obtained within a ± 0.1 mg for each sample. Since care was taken in this study to insure that all samples covered the same amount of lid surface area, the mass was taken as a relative measure of the thickness of the sample. Because this is a study of a photopolymerization process, the ability of the UV light to penetrate the sample can become the key parameter, rather than mass, at sufficiently high sample thickness.

The high and low shutter times or exposure times selected for this experiment were 25.2 s and 15.0 s, respectively. In determining what shutter times would be appropriate, many preliminary experiments were run to determine the minimum time required to insure that the resulting crosslinked polymer samples were polymerized and crosslinked (“cured”) beyond a “tacky” or “wet” state. The shutter times required to generate UV energy densities (“UV doses”) sufficient to insure non-tacky samples, of course, were dependent on the irradiance of the UV light utilized. Thus, irradiance values were selected first and were approximately 32 and 62 mW/cm^2 . **Figure 2** gives a graphical representation, in terms of the independent variables, of the experimental design used for this project.

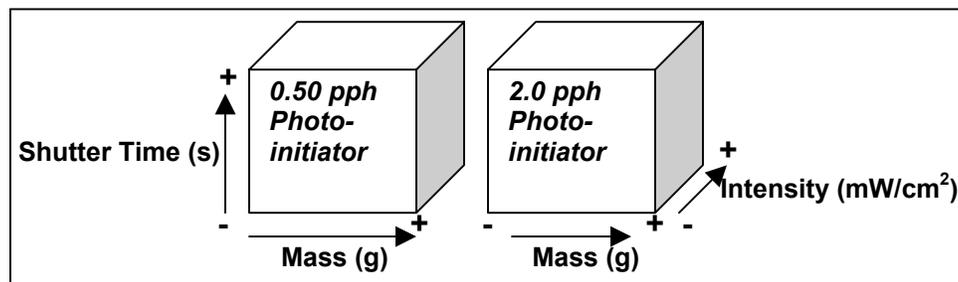


Figure 2
Graphical Representation of 2^4 -Factorial Experimental Design

RESULTS AND DISCUSSION

Although the factorial design allows one to obtain estimates of standard error without using replicates⁴, four replicates of each of the 16 planned experiments were run in order to more effectively evaluate the variability of the DPC method and to insure greater accuracy. The 48 different samples were run in random order to minimize or eliminate systematic errors and the resulting exotherm curves were then analyzed. Since only four samples were run for each experiment, the median rather than the mean of each set of results was used to evaluate the effects. It is generally accepted that for small numbers of samples, the median provides a statistically better value than the mean, which is all too easily influenced by the value of a single measurement. The medians for the dependent variables for each of the 16 experiments are given in **Table 1** along with the high and low values for the four independent variables.

From the data generated in this experiment, the main, two-factor, three-factor, and four-factor interaction effects of the independent variables on each of the dependent variables were calculated, using the median of each set of four replicates. This was done using a “Table of

Contrast Coefficients” method discussed by Box, Hunter, and Hunter⁶. In order to use this method, the data must be arranged in a “standard order.” A 2⁴-factorial design is in standard order when it is arranged as in **Table 1**. This refers to the order of the plus (+) and minus (-) independent variable values from top to bottom and left to right.

Table 1
Median Value Results of 2⁴-Factorial Design Experiment
[- Symbolizes lower-end condition and (+) Symbolizes higher-end condition]

Experiment Number	Sample* Thickness/ Mass (mg)	Shutter* Time (s)	PI Level* (pph)	Irradiance* (mW/cm ²)	Induction Time (s)	Peak Max Time (s)	Total Exotherm (J)	Peak Height (mW)
1	(-) 2.05	(-) 15.0	(-) 0.5	(-) 32.3	1.285	1.535	0.443	93.05
2	(+) 4.00	(-) 15.0	(-) 0.5	(-) 32.3	1.405	1.715	0.917	189.7
3	(-) 2.05	(+) 25.2	(-) 0.5	(-) 32.3	1.30	1.520	0.522	108.3
4	(+) 4.05	(+) 25.2	(-) 0.5	(-) 32.3	1.36	1.610	1.058	201.65
5	(-) 2.00	(-) 15.0	(+) 2.0	(-) 35.4	0.565	1.205	0.536	141.8
6	(+) 4.05	(-) 15.0	(+) 2.0	(-) 35.4	0.595	1.325	1.078	249.35
7	(-) 1.95	(+) 25.2	(+) 2.0	(-) 35.4	0.47	1.200	0.570	151.2
8	(+) 4.00	(+) 25.2	(+) 2.0	(-) 35.4	0.65	1.270	1.195	263.85
9	(-) 2.05	(-) 15.0	(-) 0.5	(+) 62.6	0.70	1.220	0.536	133.15
10	(+) 4.00	(-) 15.0	(-) 0.5	(+) 62.6	0.81	1.260	0.959	225.2
11	(-) 1.95	(+) 25.2	(-) 0.5	(+) 62.6	0.68	1.190	0.549	135.35
12	(+) 4.00	(+) 25.2	(-) 0.5	(+) 62.6	0.815	1.355	1.028	227.65
13	(-) 1.95	(-) 15.0	(+) 2.0	(+) 61.4	0.295	1.025	0.509	159.05
14	(+) 3.95	(-) 15.0	(+) 2.0	(+) 61.4	0.33	1.140	1.131	293.35
15	(-) 1.95	(+) 25.2	(+) 2.0	(+) 61.4	0.195	1.025	0.547	157.9
16	(+) 4.00	(+) 25.2	(+) 2.0	(+) 61.4	0.33	1.140	1.179	299.4

* *Independent Variables*

Table 2 shows the relative main effects of each of the independent variables. The signs indicate the direction of the relative effects, a positive sign indicating that the independent variable has the tendency to increase the value of the dependent variable, and a negative sign indicating that the independent variable tends to reduce the value of the dependent variable. The magnitude of the main effect gives an indication of how strongly a given independent variable affects the dependent variable, relative to the other independent variable effects. For example, **Table 2** shows that of the four independent variables, the photoinitiator level has the greatest effect on the induction time while the shutter time, apparently, has a negligible effect on this dependent variable.

Table 2 also shows the standard error associated with each relative main effect observed. These were calculated in accordance with a very simple procedure outlined by Box, Hunter, and Hunter that was based on an assumption that the three- and four-factor interactions are negligible⁴. As indicated in **Table 4**, this assumption proved to be true in this study, indicating that the measured differences in these interactions are a result primarily of experimental error.

The calculation of the standard error allows the significance of each relative effect to be determined. In this study, calculations were made to determine the ratio of the standard errors to their respective median response values. These ratios were then converted to percentages and ordered from the lowest to the highest. This method allows the most significant effects to be determined in rank order. Going down the listing for the results of this study, one finds that

percentage values for standard errors group together into sets, more-or-less, with a large gap between values below 25% standard error with respect to the median and values above this percentage. Thus, effects above 25% in this study were considered to be insignificant.

Table 2
Relative Main Effects With Corresponding Dependent
Variable Standard Errors (*Degrees of Freedom = 5*)

Variable (s)	Sample Thickness/ Mass (1)*	Shutter Time (2)*	Photoinitiator Level (3)*	Irradiance (4)*
Induction Time (s)	<i>0.101 ± 0.019</i>	- 0.023 ± 0.019	<i>- 0.616 ± 0.019</i>	<i>- 0.434 ± 0.019</i>
Peak Max Time (s)	<i>0.112 ± 0.020</i>	- 0.014 ± 0.020	<i>- 0.259 ± 0.020</i>	<i>- 0.253 ± 0.020</i>
Peak Height (mW)	<i>108.794 ± 3.550</i>	7.581 ± 3.550	<i>50.231 ± 3.550</i>	<i>29.019 ± 3.550</i>
Total Exotherm (J)	<i>0.542 ± 0.013</i>	<i>0.067 ± 0.013</i>	<i>0.092 ± 0.013</i>	0.015 ± 0.013

*This number in Tables 3 and 4 represents this particular independent variable.

Applying this standard to the relative main effects in **Table 2** indicates that of the 16 effects depicted, 12 are likely to be significant. These 12 main effects are shown in ***bold italics*** in the table.

Before interpreting these 12 main effects, however, it is important to determine whether or not any two-factor interactions among the independent variables are significant. **Table 3** shows the two-factor interactions with their standard errors. The only two-factor interactions that appear to have measurable effects are the interaction between UV irradiance and photoinitiator level (**3x4**) for induction time, and the sample mass and photoinitiator level for the peak height (**1x3**). According to Box, Hunter, and Hunter, the main effects of an independent variable should only be interpreted separately when there is no evidence of an interaction with other independent variables⁸.

The UV irradiance and photoinitiator level seem to have a joint effect on the induction time. However, this result is questionable since the sign of this two-level interaction is opposite that of the two main effects and its relative standard error is three or four times as great as the standard errors for the two main effects. Thus, this particular two-factor interaction is questionable and it seems more reasonable to interpret the two relative main effects separately in this case. If this interaction is considered significant, then it indicates that increases in these two parameters separately cause a decrease in the time required for inhibition to be overcome, while together it causes the process to take longer. Since increases in either one of the variables should produce a higher concentration of radicals, it is expected that increasing both of them would, in fact, cause the inhibiting factors to be overcome even more quickly.

The "**1x3**" interaction effect, on the other hand, does have the same sign as the individual main effects, but also has a much higher percentage standard error of its median value than either main effect. In fact it has twice the percentage standard error of the "**3x4**" interaction already discussed, but falls well below the percentages of the other two-factor interactions shown in **Table 3**. Thus, one must judge carefully as to whether to interpret the results based on the individual main effects or the two-factor interaction effects in this case. In this study, the main effects are interpreted for these two independent variables.

Effects on Induction and Peak Max Times - Table 2 indicates that the induction time and peak max time are most affected by the UV irradiance and the photoinitiator level. This is fully expected in light of the fact that both of these parameters directly affect the rate of generation of free radicals in the system. As the UV irradiance and photoinitiator levels are raised, more free radicals are generated in a given period of time that will react with inhibiting species, in the case of induction time, and with acrylate-functionality in the case of the peak max time. This, of course, would reduce the time required for both of these stages of the reaction.

Table 3
Two-Factor Interactions With Corresponding Dependent Variable Standard Errors (Degrees of Freedom = 5)

Variable	1x2	1x3	1x4	2x3	2x4	3x4
Induction Time (s)	0.027 ± 0.019	- 0.006 ± 0.019	0.003 ± 0.019	- 0.012 ± 0.019	- 0.006 ± 0.019	0.152 ± 0.019
Peak Max Time (s)	- 0.002 ± 0.020	- 0.007 ± 0.020	- 0.003 ± 0.020	- 6.250x10 ⁻⁴ ± 0.020	0.031 ± 0.020	0.086 ± 0.020
Peak Height (mW)	1.156 ± 3.550	15.206 ± 3.550	6.244 ± 3.550	- 0.381 ± 3.550	- 5.194 ± 3.550	- 3.144 ± 3.550
Total Exotherm (J)	0.026 ± 0.013	0.064 ± 0.013	- 0.003 ± 0.013	- 0.008 ± 0.013	- 0.025 ± 0.013	- 0.018 ± 0.013

There also appears to be a relative main effect of the sample thickness/mass variable on the induction and peak max times, but one that is opposite of and smaller than the effect of the irradiance and/or the photoinitiator levels. This is best explained by assuming that for thicker samples, the photons have more difficulty getting through to the lowest layers of the sample. If so, the overall concentration of radicals will be lower than in thinner samples, causing a lengthening of the induction and peak max times (a reduction in reaction rate).

In contrast to the other three, the shutter time variable has little or no effect on the concentration of radicals. Therefore, it would not be expected to produce measurable effects on the induction time or peak max time and no such effects were apparent.

Table 4
Three-Factor and Four-Factor Interactions With Corresponding Dependent Variable Standard Errors (Degrees of Freedom = 5)

Variable	1x2x3	1x2x4	1x3x4	2x3x4	1x2x3x4
Induction Time (s)	0.036 ± 0.019	0.004 ± 0.019	- 0.013 ± 0.019	- 0.009 ± 0.019	- 0.017 ± 0.019
Peak Max Time (s)	-0.011 ± 0.020	0.033 ± 0.020	0.013 ± 0.020	- 0.016 ± 0.020	- 0.021 ± 0.020
Peak Height (mW)	1.919 ± 3.550	0.706 ± 3.550	7.656 ± 3.550	0.444 ± 3.550	- 0.181 ± 3.550
Total Exotherm (J)	- 0.003 ± 0.013	- 0.010 ± 0.013	0.024 ± 0.013	0.009 ± 0.013	- 0.008 ± 0.013

Effects on Peak Height - The third kinetic parameter evaluated in this study was the peak height. As previously mentioned, the maximum height of the exotherm curve represents the point in the polymerization when the rate of the reaction is at its maximum. For this dependent

variable, not only did the UV irradiance and photoinitiator level exhibit an effect, but also the sample thickness/mass variable had a very substantial effect. **Table 2** indicates that all three independent variables created a positive response in the peak height indicating that increases in any of them produce a higher maximum reaction rate. **Table 3** also indicated a relatively small two-factor interaction between the sample thickness/mass and the photoinitiator level. This two-factor effect was much smaller than any of the three main effects and had a substantially larger percentage standard error, as previously mentioned. Thus, it seems more appropriate to interpret the separate main effects rather than this one two-factor interaction effect.

The effects of UV irradiance and photoinitiator level on the maximum reaction rate (peak height) are completely predictable, as with the other two kinetic dependent variables. The effect of the sample thickness and/or mass on the peak height, however, is a little more difficult to understand. At a critical sample thickness, one might expect to see a negative effect on reaction rate due to the difficulty of getting the UV light all the way through the sample to its lower layers. In fact, such an effect was evident with the induction and peak max times, though the effect was quite small, possibly indicating that the sample thickness was very close to some critical thickness where light would be significantly impeded. However, for the sample thickness/mass variable, there was a substantial positive effect on the maximum rate of the reaction.

Rather than the thickness, then, it would appear that the mass of the sample should be considered in interpreting the observed peak height effect. Assuming reasonably effective passage of the UV light through the sample, a larger mass sample would produce more total thermal energy during the exotherm. Although ideally, the reaction should be run in the DPC unit under isothermal conditions, in reality there is some increase in the temperature of the sample during polymerization, just as there is when materials are undergoing UV polymerization on commercial production lines. This increase in temperature would be expected to give a “thermal boost” to the reaction rate, causing the maximum observed rate of polymerization to increase. On a relative significance basis, this mass effect is more than twice the effect of the photoinitiator level and 3.7 times higher than the effect of the UV irradiance. In fact, the mass effect on the peak height is overwhelmingly the largest single effect observed in this entire investigation.

Total Exotherm - Table 2 shows that three of the four independent variables had significant effects on the total exotherm. The sample thickness/mass effect had the largest relative significance with a median value nearly six times higher than that of the photoinitiator level and about eight times higher than that of the shutter time. As discussed previously, when the sample mass increases, the evolution of more energy is expected, assuming the sample thickness remains below a level that would preclude photons from penetrating to the lowest layers of the sample.

The photoinitiator concentration also seemed to have a measurable effect on the total exotherm experienced. Since a higher concentration of photoinitiator would lead to a higher concentration of radicals, a higher conversion of monomer to polymer would be expected, causing more total energy to be evolved from the reaction.

The shutter time variable had no significant effects on any dependent variable except the total exotherm. Since the time the shutter is open has nothing to do directly with the generation radicals, one would not expect it to have substantial effects on the three kinetic parameters. On the other hand, one would expect to see an effect on total exotherm since exposing the sample to UV light for a longer period of time increases the UV energy density. This means that each square centimeter of the sample surface would receive a higher total number of photons. This should result in a higher number of radicals being formed and a higher percentage of the acrylate double bonds being converted to polymer. Between systems that contain the same amount of acrylate functionality, the one that has a higher percent conversion should produce a higher total exotherm.

The fact that the shutter time exhibited no significant effects on any of the other dependent variables is also not surprising. This lack of apparent effect indicates that even at the lower 15-second shutter time, virtually all of the reactions were very near completion by the time the shutter closed. **Figure 1** shows a typical exotherm scan where the shutter is opened after 30 seconds of equilibration. One can see from the scan that for a shutter time of 15 seconds, the shutter would be closing at 45 seconds into the experiment. This is well past the induction time, the peak max time, and the peak height. Therefore, even at the 15-second shutter time, the three kinetic dependent variables have all responded on an essentially complete basis. Thus, to more effectively evaluate the effect of shutter time on the kinetic variables, an experiment is needed that involves a low-end shutter time of something less than the peak max time for the systems being investigated. This would, in turn require a higher UV irradiance for these systems to insure that sufficient UV energy density is available to “cure” the samples to a tack-free state.

It is a bit surprising that the total exotherm was not significantly influenced by the UV irradiance. Higher numbers of photons per second striking the sample should produce a higher concentration of radicals at all stages of the polymerization and this, in turn, should increase the reactivity of the system. This rate effect of the irradiance is evident with all three kinetic variables evaluated in this investigation. It might be assumed that a faster rate of reaction would automatically lead to a higher conversion of monomer to polymer, resulting in a higher total exotherm. However, this is not necessarily true. Increasing the reactivity of a system may simply decrease the time necessary for the system to achieve its ultimate crosslink density before vitrification and gelation cause radicals and functional groups to become trapped and, thus, unreacted⁹. Unless a higher percentage of functional groups are reacted, there would not be an increase in the total exotherm observed.

SUMMARY AND CONCLUSIONS

The results of this study demonstrate the value of DPC technology for determining the kinetic and thermodynamic properties of UV-polymerizable formulations. Using a 2⁴-factorial experimental design, an assessment was made of the effects of sample thickness (mass), shutter time, UV irradiance, and photoinitiator concentration on the induction time, peak max time, peak height, and total exotherm of two UV-polymerizable formulations. This experimental design worked very well and provided a lot of information about the effects of the four independent variables on the four dependent variables, using a relatively few experiments.

The results indicated that sample thickness, UV irradiance, and photoinitiator concentration all had effects on the induction time and the peak max time but the sample thickness seemed to decrease the reactivity while the other two independent variables increased it. This is consistent with the fact that only the photoinitiator level and the irradiance have a direct effect on the free radical concentration in the polymerizing systems. The sample thickness effect appeared to be a result of the sample thickness being very near to a critical thickness beyond which the UV light would have trouble penetrating all the way to the lowest layers of the sample. Assuming this to be true, the thinner samples would have more effective radical formation and, thus, would be higher in reactivity than the thicker samples.

The peak height, on the other hand, seemed to be influenced by the sample's mass, rather than its thickness, as well as the UV irradiance and the photoinitiator level. Since sample mass does not directly affect the concentration of radicals, this effect, most likely, results from the expected and observed effect of mass on total exotherm. Because the reactions were not run under perfectly isothermal conditions, the resulting increase in temperature with higher mass, probably gave a significant "thermal boost" to the reaction, causing the maximum rate of reaction to increase substantially.

Finally, the total exotherm was affected positively by the sample mass, the shutter time, and the photoinitiator level. It is assumed that the higher photoinitiator level produced a higher concentration of radicals that, in turn, generated a higher percent conversion of acrylate double bonds to crosslinked polymer. Why a similar effect on total exotherm was not observed for the UV irradiance is not clear. Perhaps the absolute difference between the lowest irradiance value and the highest was not sufficiently large for this particular effect to be observed.

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REFERENCES

1. More, James E., "Calorimetric Analysis of UV Curable Systems", Pappas, S. Peter, Ed., *UV Curing: Science and Technology*, pp. 133-159 (1978).
2. Hoyle, Charles E., "Calorimetric analysis of Photopolymerization", Pappas, S. Peter, Ed., *Radiation Curing*, pp. 57-133 (1992).

3. Box, Hunter, and Hunter, *Statistics for Experimenters*, John Wiley & Sons, Inc., 1978, p. 306.
4. Box, Hunter, and Hunter, *Statistics for Experimenters*, John Wiley & Sons, Inc., 1978, p. 327.
5. Box, Hunter, and Hunter, *Statistics for Experimenters*, John Wiley & Sons, Inc., 1978, pp. 306-351.
6. Box, Hunter, and Hunter, *Statistics for Experimenters*, John Wiley & Sons, Inc., 1978, pp. 322, 326.
7. Box, Hunter, and Hunter, *Statistics for Experimenters*, John Wiley & Sons, Inc., 1978, pp. 317, 318.
8. Selli, E. and Bellobono, I., "Photopolymerization of Multifunctional Monomers: Kinetic Aspects", *Radiation Curing in Polymer Science and Technology Volume III: Polymerization Mechanisms*, J. P. Fouassier and J. F. Rabek, eds., Elsevier Applied Science, 1993, pp. 10-14.