# Optical Pyrometry: A New Method for Monitoring Photopolymerizations

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## Abstract

Optical pyrometry (OP) is a new, rapid, reproducible, versatile and inexpensive technique for continuously monitoring free radical and cationic photopolymerizations. OP can be employed to examine the effects of many different experimental and compositional variables of photopolymerization reactions. The OP technique can be utilized in fundamental studies of photopolymerizations as well as for the rapid optimization of the multicomponent photopolymerizations used in practical applications. Furthermore, OP may be used as a valuable quality control/product assurance technique for ensuring the reactivity of photocurable formulations.

## Introduction

Photopolymerizations are becoming increasingly important for many industrial applications. Since these polymerizations are performed in the absence of a solvent, there is little or no volatile organic compounds (VOC) released, which is becoming increasingly important as stricter government emission regulations are enacted. Photopolymerizations are extremely rapid reactions, occurring in fraction of a second to several minutes. The short time scale of these reactions makes it difficult to monitor their kinetics. A variety of analytical techniques have been developed. The two most widely used are real time infrared spectroscopy (RTIR), developed by Decker,[1-3] and differential scanning photocalorimetry (DSP)[4]. These methods work well when the system under study is a simple formulation consisting of one or two monomers. More complex formulations make the analysis of the data difficult. Also, the cost of the RTIR ($30,000) and DSP ($100,000) instrumentation is high. Another limitation of RTIR and DSP is that photopolymerizations cannot be studied on the substrates on which they will be applied. We have developed a novel analytical technique called optical pyrometry[5,6] (OP) to study the course of photopolymerizations. The following article describes the use of an optical pyrometer to directly and remotely monitor the temperature of a monomer sample while it is undergoing photoinduced polymerization.

## Experimental

Materials

Commercial monomers used in this investigation were purified by drying, vacuum distillation, or by passing the monomers through a column of activated alumina. Triethyleneglycol divinyl ether (DVE-3) was a gift of the International Specialties Corp. (Wayne, NJ). 3,4-Epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (ERL-4421E) was obtained from Union Carbide Corp. (Bound Brook, NJ). PC-1000 was a gift from the Polyset Co. (Mechanicville, NY). 3-Oxetanylmethyl)phenyl ether (POX) and bis(3-ethyl-3-oxetanylmethyl ether (DOX) were gifts from the Toagosei Chemical Co. (Nagoya, Japan). The silicon-containing monomers were prepared as previously described.[7] All other monomers

were purchased from the Aldrich Chemical Co. (Milwaukee, WI). The free radical photoinitiators were gifts from Ciba-Geigy Corp. (Tarrytown, NY). The pigments were obtained from the following sources: Permanent Red 2B-220 and Phthalo Blue 41611 from Peer Chemical Corp. (Wheeling, IL), and titanium dioxide from Kronos, Inc. (Houston TX). Cationic photoinitiators: (4-n-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10),[8] (4-*n*-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate (SOC10)[9] and *S*-*n*-dodecyl-*S*-methyl-*S*-phenacylsulfonium hexafluoroantimonate (DPS)[10] were prepared as previously described.

Optical Pyrometry (OP)

Figure 1 shows a schematic drawing of the "stand alone" optical pyrometry apparatus. An unmodified OS552-V1-6 Industrial Infrared Thermometer was used as obtained from Omega Engineering, Inc., Stamford, CT. This instrument is capable of reading temperature to ± 1 °F at 1 data point per second. The sample was placed 15.2 cm from the OP camera. At this configuration the sensing diameter is 3.9 mm. A UVEX model SCU-110 mercury arc lamp fitted with a 95 cm liquid light pipe was used to deliver the UV light to the sample. The temperature and time data was recorded using an IBM 350-P137 personal computer and to plotted using EXCEL software. The humidity of the chamber was adjusted by first passing compressed air through a desiccant column or a column of water.
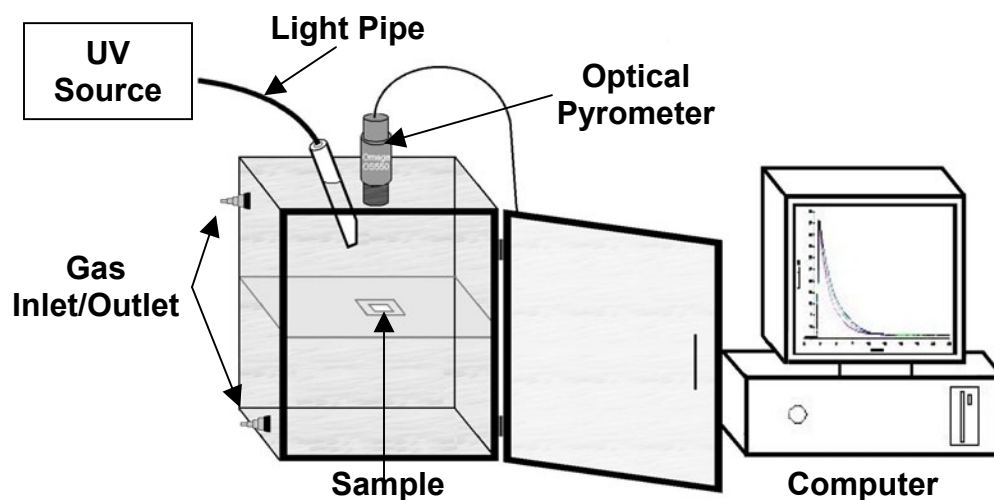


**Figure 1    Schematic of the "stand alone" optical pyrometer.**

The monomer samples were prepared as follows. A thin fiber mesh was first placed onto a 10 μm corona treated polypropylene film. Then the monomer solution was added and a second polypropylene film was placed on top. Finally, this assembly was placed into a plastic 2 cm x 2 cm slide holder. In this way, a uniform sample thickness of 0.912 mm was obtained. The sample was placed into the sample holder of OP instrument and the temperature was allowed to equilibrate for 20 seconds prior to UV exposure. Photopolymerizations were carried out at ambient temperature. A comprehensive description of the OP apparatus and operating procedures can be found in a previously published paper.[5]

# Results and Discussion

Optical pyrometry (OP) is a technique developed in this laboratory to compare the rapid kinetics of various photopolymerizable systems. Shown in Figure 2 are the thermograms obtained when 4-vinyl-1-cyclohexene dioxide (VCHDO) was photopolymerized using a diaryliodonium salt as the cationic photoinitiator. Multiple runs of this sample were compared and the thermograms are nearly identical. Since this cationic photopolymerization, like all chain growth polymerizations, is exothermic, the rapid conversion of monomer to polymer is accompanied by an increase in temperature. The temperature attained by the thin film sample in just a few seconds is over 370 $^{\circ}$C. The system exhibits a typical induction period followed by a rapid rise in temperature that is characteristic of an autoacceleration effect.
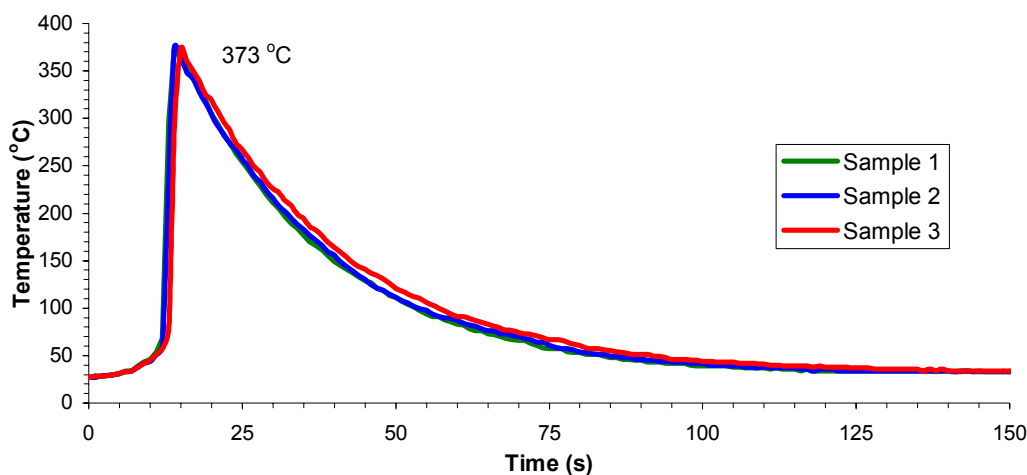


**Figure 2** **Thermograms of the cationic photopolymerization of 4-vinyl-1-cyclohexene dioxide (VCHDO) using a 1.0 mol% (4-n-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10 SbF$_6^-$) as the photoinitiator (light intensity: 395 mJ/cm$^2$·min).**

To examine the correlation between the temperature rise and conversion we have performed simultaneous real-time infrared spectroscopy (RTIR) and OP measurements on the same sample. The experimental apparatus used for these measurements is shown in Figure 3. The samples were prepared in the same fashion as the "stand alone" OP apparatus, then placed in the sample holder of the RTIR spectrometer. The OP camera was placed 15.2 cm away from the sample and at a 45$^{\circ}$ angle. The ultraviolet (UV) source was turned on while two separate computers were used to simultaneously record the sample temperature and the monomer conversion as a function of time.
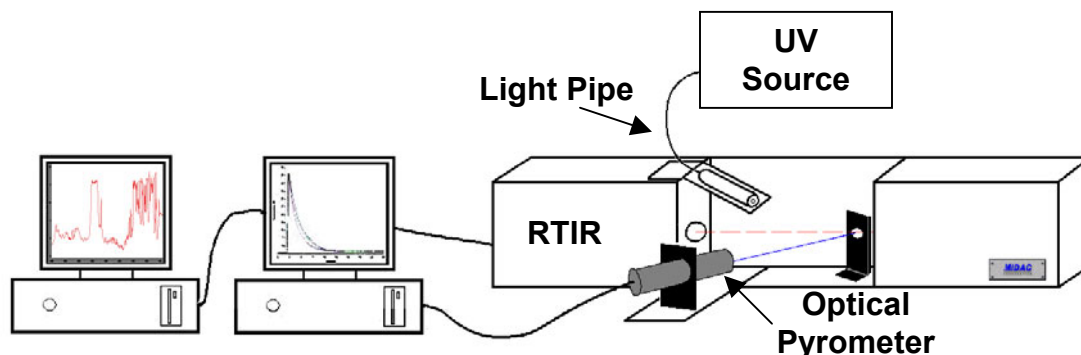


**Figure 3** **Schematic of the combined optical pyromter and real time infrared spectrometer.**

Shown in Figure 4 is a combined RTIR and OP study of the photopolymerization of VCHDO with 1.0 mol% (4-n-decyloxyphenyl)phenyliodonium hexafluorophosphate (IOC10 PF$_6$) as the photoinitiator. There is an obvious direct relationship between monomer consumption and the rise in temperature. The induction period observed by both analytical techniques is identical. The time required to reach both the maximum rate of monomer conversion and the maximum change in temperature are also identical. As the monomer is depleted, the rate of polymerization, and temperature simultaneously decrease. When polymerization ceases, the sample begins to rapidly cool.
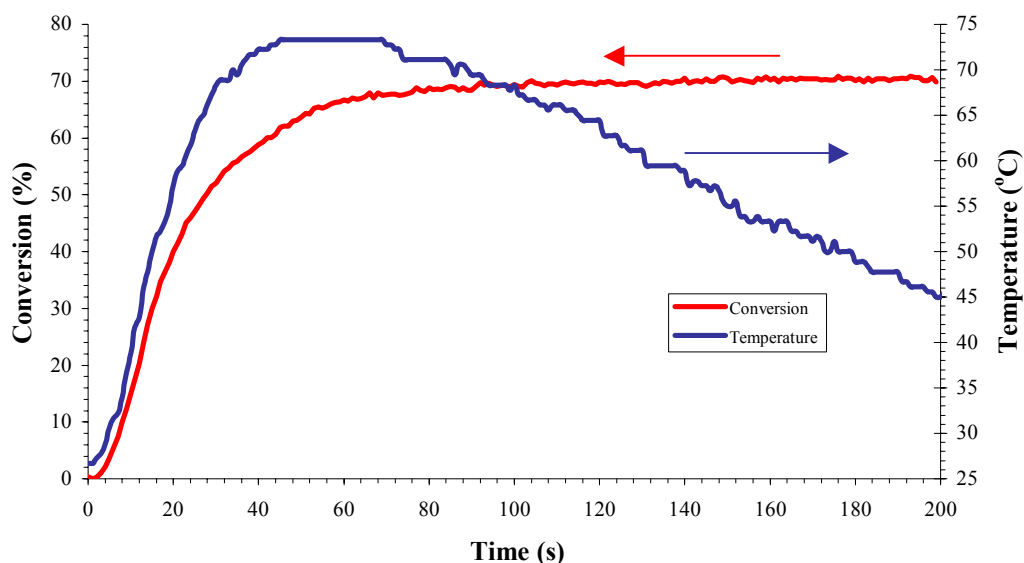


**Figure 4    Combined RTIR and OP study of VCHDO and with 1.0 mol% (4-n-decyloxyphenyl)-phenyliodonium hexafluorophosphate (IOC10 PF$_6$) (light intensity: 999 mJ/cm$^2$·min)**

Observation of the Effects of Reaction Variables by OP

Temperature profiles for the radical photopolymerizations of four different monomers are depicted in Figure 5. Diethylene glycol diacrylate (DEGDA) shows the most rapid temperature increase. Ethylene glycol dimethacrylate (EGDMA) exhibits the slowest rate. Hoyle et al.[11] have shown that methacrylates polymerize at a slower rates then the corresponding acrylates. This due to the greater steric hindrance of the methacrylate double bond. The reactivity of 1,6-hexanediol diacrylate (HDODA) is slightly less than DEGDA and bisphenol A diglycidyl ether diacrylate (BPADA) shows moderate reactivity at best.

The reactivity of three structurally different difunctional epoxy monomers were assessed by OP and the results are shown in Figure 6. To obtain a thermogram with a sufficient signal to noise ratio, the light intensity was increased from ~400 mJ/cm$^2$·min for VCHDO and PC1000 to 1100 mJ/cm$^2$·min for ERL4221E. The rate of polymerization of VCHDO and PC1000 is clearly more rapid than that of ERL4221E. Even when the light intensity is more than doubled the reactivity of ERL4221E is relatively poor. ERL4421E is used as the "work horse monomer" in many cationic photopolymerization applications. The slow rate of polymerization of ERL4221E is attributed to interactions of the growing chain and the ester group of the monomer, which reduces the rate of propagation.
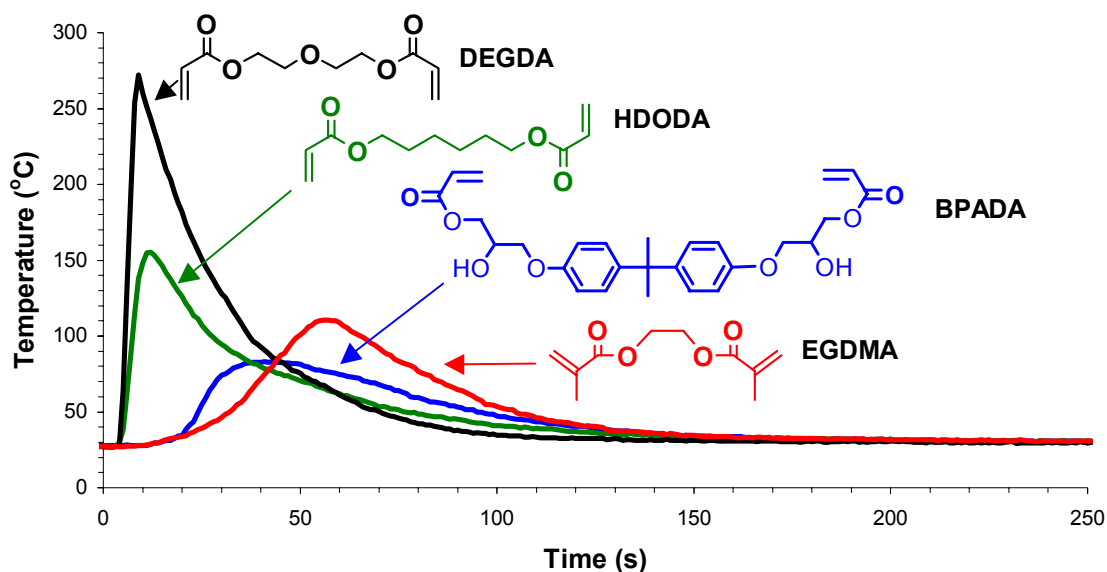
**Figure 5** Various free radical monomers photopolymerized using 1 mol% 1-benzoyl-1-hydroxycycloxhexane (Irgacure 184®) (light intensity: 400 mJ/cm²·min ).
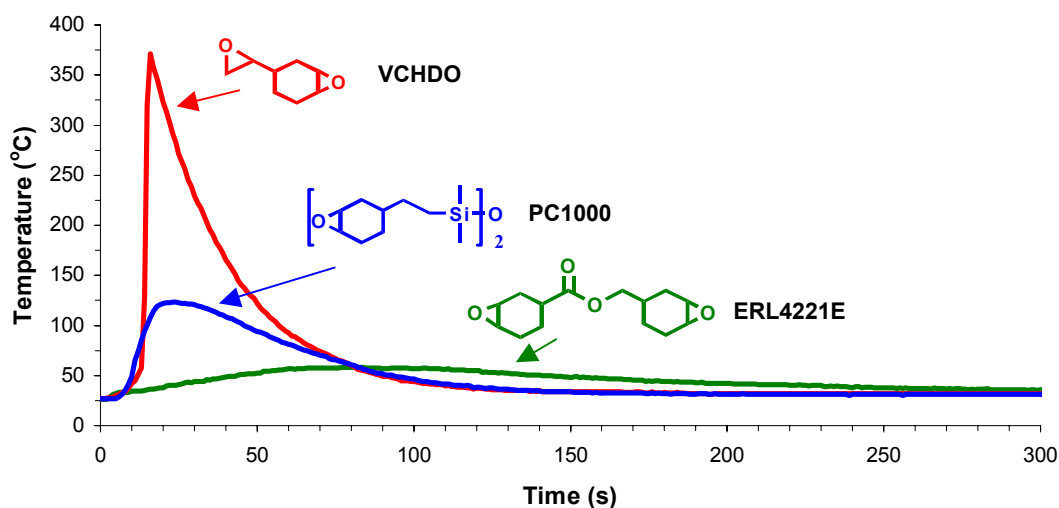


**Figure 6** Thermal profiles for the cationic photopolymerizations of three different difunctional epoxide monomers. VCHDO, 0.25 mol%, 395 mJ/cm²·min IOC 10; PC1000, 0.25 mol% IOC 10, 380 mJ/cm²·min; ERL4221E, 1.0 mol% IOC 10 SbF$_6^-$, 1100 mJ/cm²·min.

It is has been shown that cycloaliphatic epoxy groups undergo a more facile acid catalyzed ring-opening polymerization as compared to analogous open-chain epoxy compounds.[12] VCHDO contains one cylaliphatic and one aliphatic epoxy group. PC1000 contains two cycloaliphatic epoxy groups. Based on ring strain alone, the rate of photopolymerization of PC1000 should be faster than that of VCHDO. However, OP studies show that the reactivity of these two monomers is reversed. It should be noted that the epoxy equivalent weight for VCHDO is 70 g while that of PC1000 is 191 g. Thus, VCHDO has more than a two-fold higher density of epoxy groups than PC1000. Each epoxy group will release 21 –105 kJ/mol[13] of energy during propagation as heat. The greater the density of functional groups, the more energy is evolved per unit mass and the higher the resultant temperature. To further examine the effect of the density of functional groups we synthesized two additional

related silicon-containing monomers.  Shown in Figure 7 are the thermograms of three monomers with identical numbers and types of epoxy functional groups.  They differ only in the length of the siloxane spacer groups.  The data in Figure 7 indicates that as length of the spacer group increases (the density of functional group decreases), the rate of polymerization decreases.
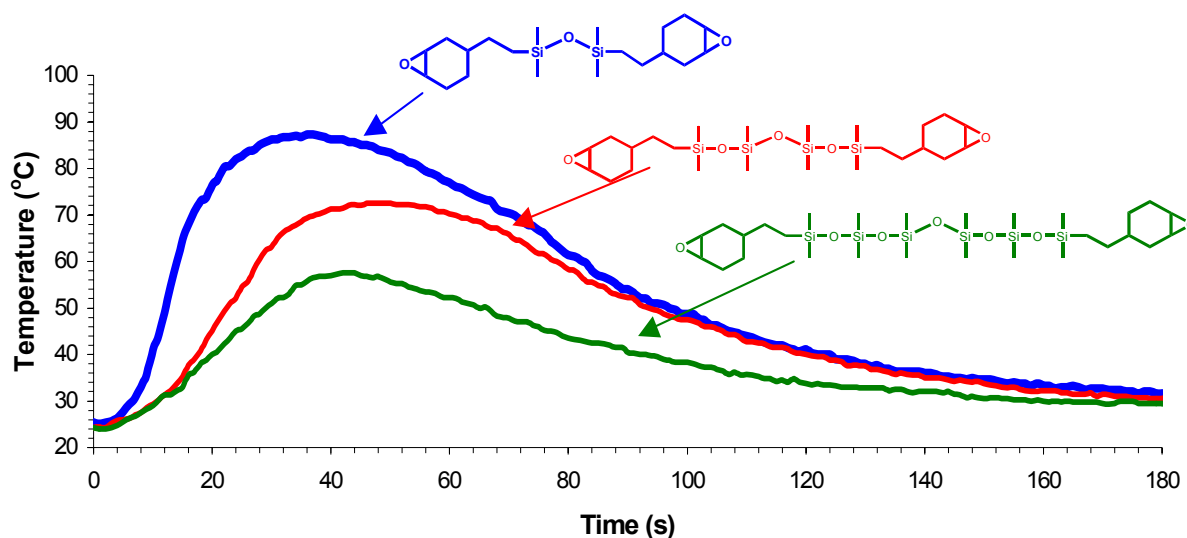


**Figure 7      Effect of siloxane space lenghth with 1.0 mol% IOC10 SbF$_6^-$ (light intensity: 497 mJ/cm$^2$·min).**

The type of photoinitiator used in a photopolymerization also influences the cure rate. The efficiencies of various photoinitiators in a given monomer system can rapidly and easily be assessed using OP.  Several commercial free radical cleavage-type photoinitiators were examined in the photopolymerization of 1,6-hexanediol diacrylate (HDODA).  The bisacylphosphine oxide photoinitiator, Irgacure 819®, is the most efficient of the series shown in Figure 8.  Analysis by differential scanning photocalorimetry (DSP)[14] and real-time infrared spectroscopy (RTIR)[15] results gave similar results.
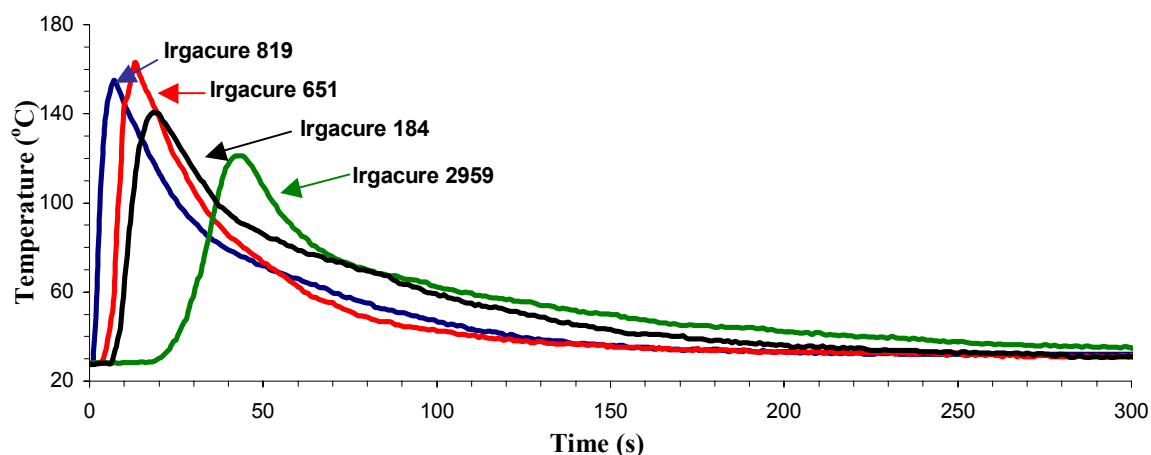


**Figure 8  Comparison of effect of various free radical photoinitiators on the photopolymerization of 1,6-hexanediol diacrylate (HDODA) (1.0 mol% photoinitiator, light intensity: 423 mJ/cm$^2$·min).**

An analogous study for cationic photoinitiators is shown in Figure 9. Three typical onium salt photoinitiators were used in the photopolymerization of PC1000 and the rates were compared using OP. The iodonium salt, IOC10 $SbF_6^-$, is the most active photoinitiator while *S-n-dodecyl-S-methyl-phenacylsulfonium* hexafluoroantimonate (DPS) displayed moderate reactivity. The relative reactivities obtained using OP are similar to the previously published rates obtained using RTIR.[10,16]
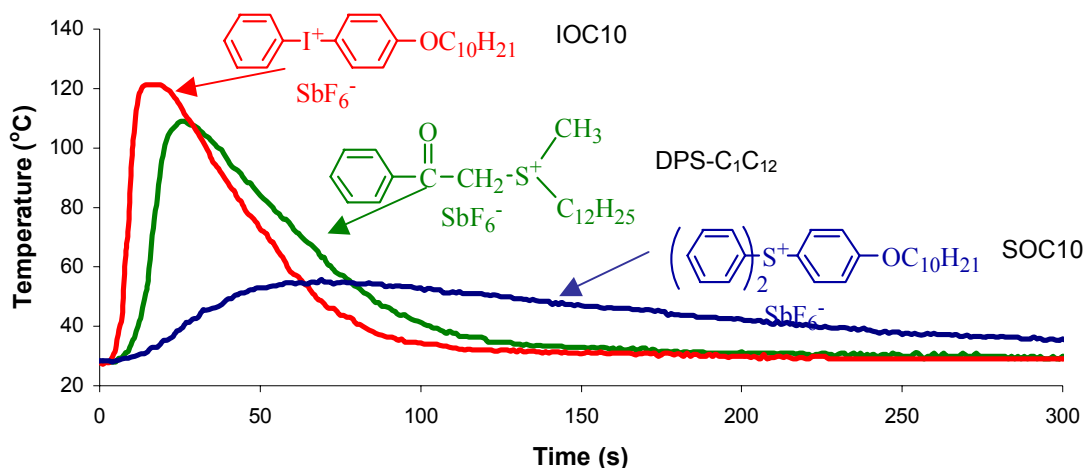


**Figure 9** **Thermal profiles of photopolymerizations employing three different photoinitiators and PC1000 as the monomer (0.25 mol% photoinitiator, light intensity: 400 mJ/cm$^2$·min).**

As in most industrial processes, it is important to reduce the cost of production by maximizing the speed or throughput of a photocurable system. The photoinitiator is the most expensive component of a photopolymerizable formulation. OP is an excellent technique for maximizing the efficacy of the photoinitiator. Shown in Figure 10 are the thermograms for the photopolymerization of PC1000 using different concentrations of IOC10 as the photoinitiator.
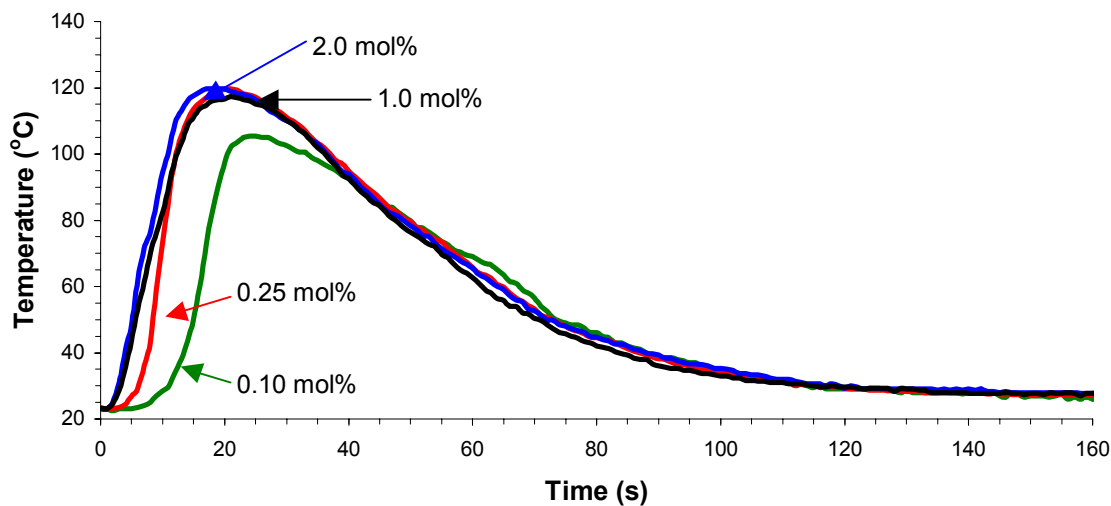


**Figure 10** **Impact of the concentration photoinitiator (IOC10 SbF$_6^-$) on the cationic photopolymerization of PC1000 (Light intensity: 408 mJ/cm$^2$·min).**

As the concentration of the photoinitiator was varied from 0.10 mol% to 1.0 mol% the rate of polymerization increases and the induction period decreases to a certain point. However, when the concentration of the photoinitiator is further increased from 1.0 to 2.0 mol% little to no change in the thermogram is observed.

Optimization of the light intensity is important to reduce the energy consumption of a photocuring process. Excess UV exposure leads to an unnecessary increase in the cost of production. Shown in Figure 11 are the thermograms of the photopolymerization of diethylene glycol diacrylate (DEGDA) and 1.0 mol% Irgacure 184® (1-benzoyl-1-hydroxycyclohexane) obtained at different light intensities. As the light intensity is increased from 100 to 495 mJ/cm$^2$·min the induction period deceases and the rate of polymerization increases. A further increase in UV exposure does not affect the rate of polymerization. Thus, for this system the optimum light intensity lies between 250 and 495 mJ/cm$^2$·min.
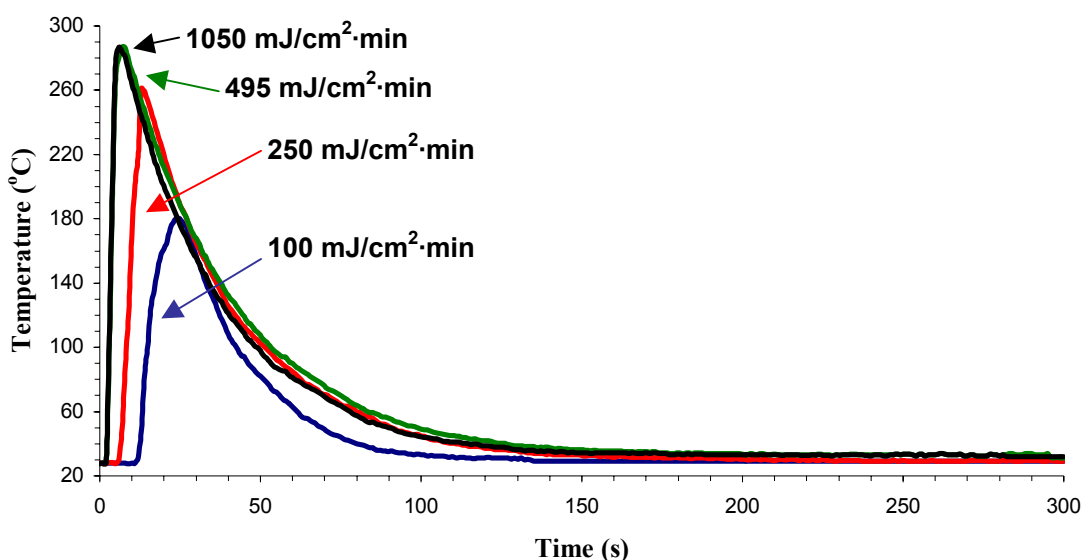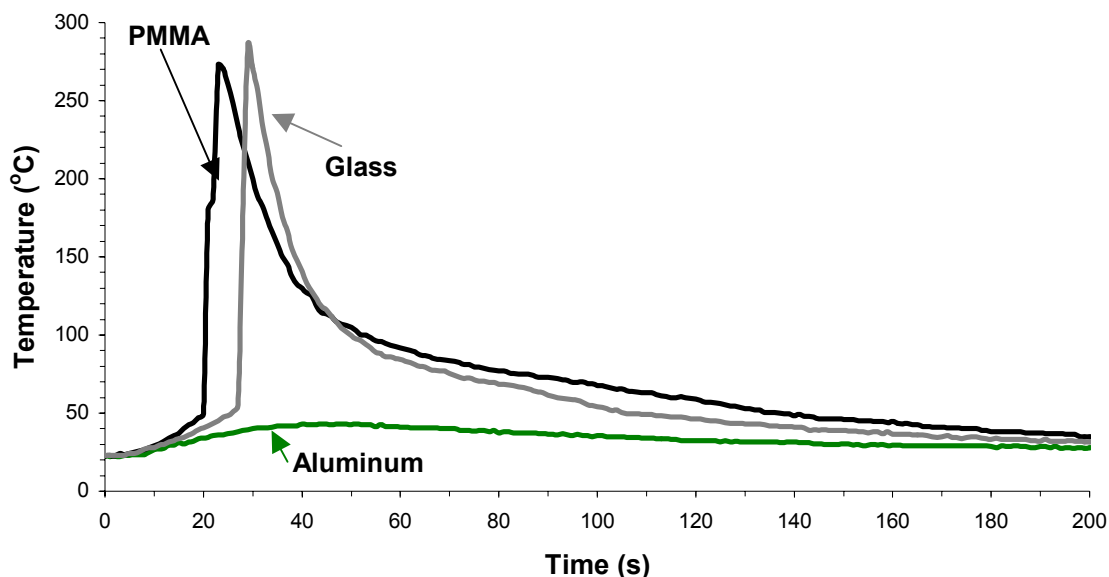


**Figure 11  Effect of light intensity on the photopolymerization of diethylene glycol diacrylate (DEGDA) (1 mol% Irgacure 184®).**

Unlike RTIR, OP does not require a sample to be transparent. This allows for the study of pigment, filler and substrate effects on the photopolymerization of various systems. Cationic systems are highly influenced by the substrate on which they are polymerized. As we have shown before in this article, cationic photopolymerizations reach a temperature where autoacceleration occurs. The thermal conductivity of the substrate plays a crucial role whether this temperature range can be attained. Figure 12 demonstrates the substrate effect on the cationic photopolymerization of VCHDO with 4-methoxybenxyl alcohol (accelerator) and 1.0 mol% IOC10 as the photoinitiator. Poly(methyl methacrylate) (PMMA) and glass have low thermal conductivities (8 X 10$^{-6}$ and 1.38 x 10$^{-2}$ W·cm$^{-1}$·K$^{-1}$ respectively). Using PMMA and glass, the temperature of the system can rise sufficiently to allow for autoacceleration to occur (~50-55 ºC). This is evident by the dramatic rise in slope and high peak temperatures. The thermal conductivity of aluminum is much higher (2.36 W·cm$^{-1}$·K$^{-1}$) as compared to glass and PMMA. The heat transfer of the system is rapid and the temperature (47 ºC) of the system does not increase sufficiently enough to induce autoacceleration. For this reason, the

photopolymerization is dramatically slowed.  OP is the first technique that allows the substrate effects to be easily examined.  A study of substrate effects on the radical photopolymerization of hexanediol diacrylate (HDODA) was also performed.   A less significant effect was seen between the thermograms of the free radical photopolymerizations obtained using the three substrates.



**Figure 12   Effect of different substrates on the photopolymerization of VCHDO with 20 mol% 4-methoxybenzyl alcohol containing 1.0 mol% IOC10 (light intensity: 1006 mJ/cm$^2$·min).**

Both free radical and cationic polymerizations are also affected by atmospheric conditions.   Oxygen is well known to inhibit free radical photopolymerizations.   The photopolymerization of a monomer solution composed of ethylene glycol dimethacrylate with 1.0 mol% Irgacure 184® was run with and without a polypropylene cover film is shown in Figure 13.   Since sample was not covered, it was exposed to air as it polymerized.   For comparison, the same sample with a cover was also photopolymerized.   This sample experienced only limited exposure to oxygen during photopolymerization.  The covered sample reached a peak temperature of 111 $^o$C while the temperature of the uncovered sample reached only 58$^o$C.

Although cationic photopolymerizations are not inhibited by the presence of oxygen, they are sensitive to atmospheric moisture.  The cationic photopolymerizations of vinyl ethers are particularly inhibited by water.  Vinyl ethers also undergo addition reactions with water to form aldehyde and alcohol side products.  This is demonstrated in the OP study shown in Figure 14 (the curves are truncated in this figure to show only the initial rise of the temperature).  Triethylene glycol divinyl ether (DVE-3) was photopolymerized under controlled relative humidity (RH) atmospheres.  The induction period was significantly extended when the relative humidity was increased from 23% to 82%.  When all of the water is consumed through addition to the vinyl ether double bonds, the polymerization proceeds rapidly.
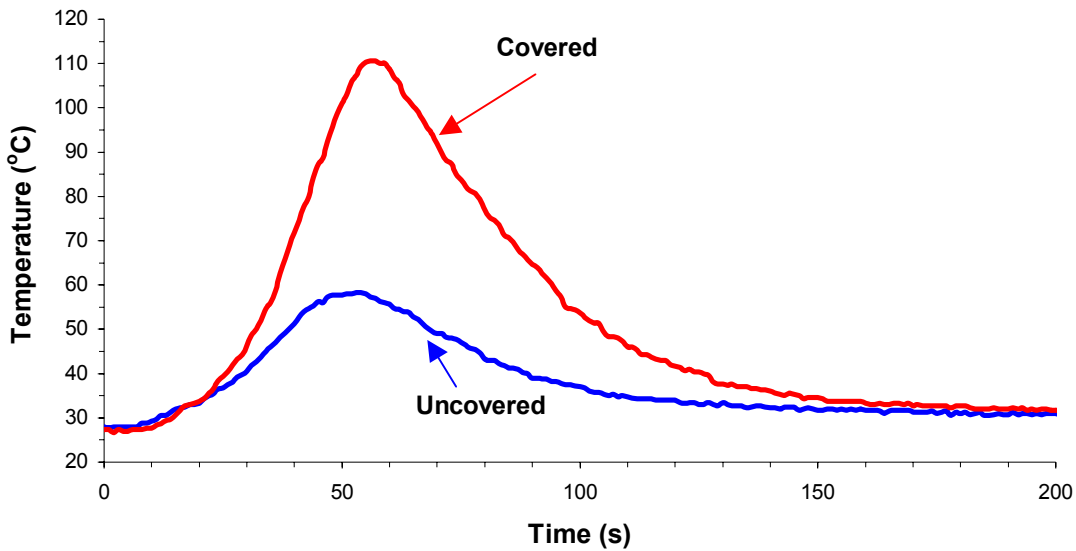
**Figure 13**   Effect of oxygen on the photopolymerization of ethylene glycol dimethacrylate (EGDMA).  (1.0 mol% Irgacure 184®, light intensity: 400 mJ/cm²·min).
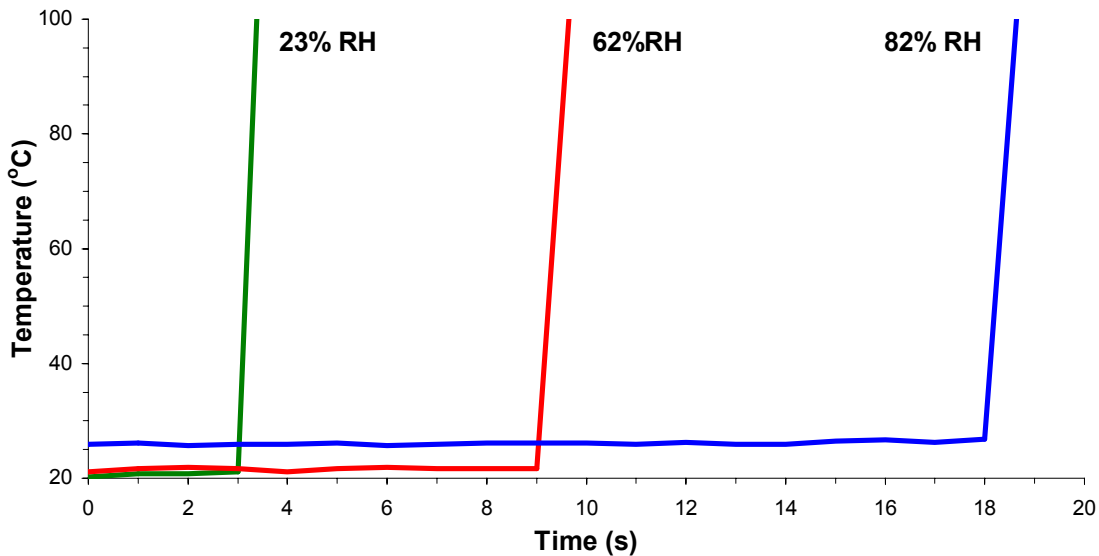


**Figure 14**   Humidity effects on the photopolymerization of triethylene glycol divinyl ether (DVE-3) (23% RH and 82% RH runs were uncovered while 62% RH run was covered; 0.5 mol% IOC15, light intensity: 315 mJ/cm²·min).

Many photocurable coating formulations include pigments.  Pigments reduce the rate of polymerization due to competitive light absorption, scattering, reflectance, and screening effects.[17,18]  Since OP does not require transparent samples, pigments do not interfere with the analysis.  Figure 15 shows the thermograms obtained when pigments are added to a solution of PC1000 with 1 mol% IOC10.  It is interesting to note that not only do the pigments reduce the rate of polymerization but also each pigment affects the rate differently.  OP can be used to adjust the formulation of these systems to account for the differences in reactivity.
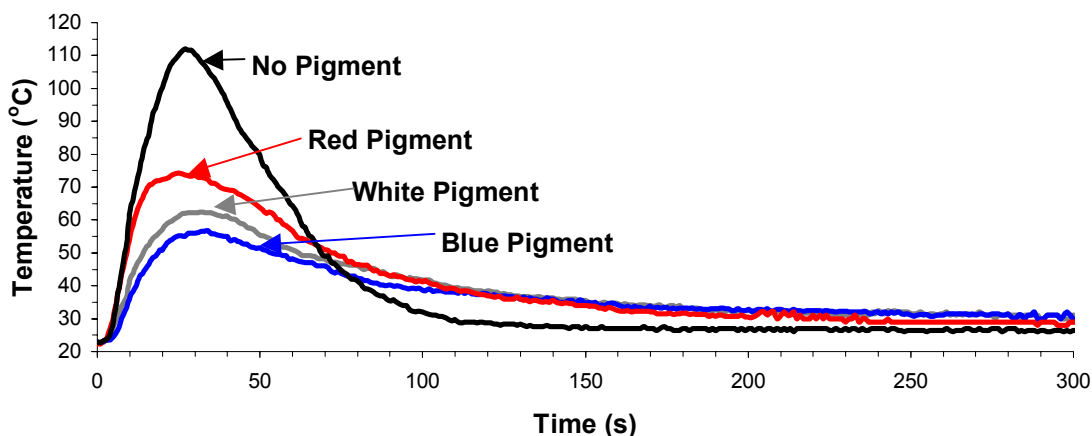
**Figure 15   Impact of pigments (1.0 wt%) on the photopolymerization of PC1000 (1 mol% IOC10, light intensity: 396 mJ/cm$^2$·min).**

## Conclusions

OP is a novel, rapid, reproducible, versatile and inexpensive technique for monitoring both free radical and cationic photopolymerizations. This technique remotely and continuously measures the temperature of a system undergoing photopolymerization. Results obtained by OP were correlated with those obtained by RTIR to show that the temperature rise in the system is directly related to the rate of polymerization. A wide variety of experimental and compositional variables of photopolymerization reactions were examined using OP. We anticipate that a variety of researchers will benefit from this technology from academic fundamental investigations to industrial optimization of multicomponent formulations. Furthermore, OP may be used to develop quality control standards to develop procedures to ensure the predicable curing behavior of industrial coatings.

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