

Head-to-head Comparison of Cationic Photoinitiator Effectiveness

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Introduction

Since their inception in 1972 by Crivello and coworkers at the General Electric Corporate Research and Development Center,¹ onium salt photoinitiators have played a pivotal role in the advancement of cationic photopolymerization. These photoinitiators are commonly used with cyclic ethers such as epoxides and oxetanes.² When the photoinitiator absorbs light, it forms a strong acid, which then interacts with the cyclic ether to form the propagating cationic active center.³ There are many benefits to using cationic photopolymerization over free-radical photopolymerization. Cationic reactions are not inhibited by oxygen like free-radical reactions and therefore do not require mitigation strategies such as nitrogen inerting, which can be expensive and cumbersome. Though photopolymerization is typically limited to thin films, cationic active centers are longer lived than free-radical active centers and can diffuse through the system, facilitating cure of thicker and/or highly filled films. However, cationic polymerization is sensitive to bases, alcohols, and water.⁴

Onium salt photoinitiators are composed of either a diaryliodonium or triarylsulfonium cation and an anionic counterion.² The cation absorbs light due to the conjugated double bonds of the aromatic rings, and its structure determines the wavelength of light absorbed. To absorb sufficient energy to initiate the polymerization, the absorbance spectrum of the photoinitiator must at least partially match the emission spectrum of the light source. The anionic counterion forms the superacid that initiates the polymerization reaction, and the strength of the superacid dictates the initiation efficiency and the rate of propagation.¹

The goal of this study was to compare the effectiveness of a variety of onium salts on an equal-absorbance basis. The absorptivity of each onium salt was quantified to determine impact of cation structure on absorbance. The absorbance spectrum of each onium salt was then compared to the emission spectrum of a commonly used mercury arc lamp. The overlap of onium salt absorbance and lamp emission was calculated to quantify the relative amount of light energy absorbed. Finally, equivalent-overlap formulations were illuminated to determine if the spectral overlap predicted monomer conversion to polymer.

Experimental

Materials

Ten onium salts (Figure 1) were chosen to compare the impact of cationic structure on absorbance characteristics and anionic structure on polymerization effectiveness: [4-(2-hydroxy-1-tetradecyloxy)-phenyl]phenyliodonium hexafluoroantimonate (IFA, Polyset); [4-(2-hydroxy-1-tetradecyloxy)-phenyl]phenyliodonium hexafluorophosphate (IFP, Polyset); bis(4-t-butylphenyl) iodonium hexafluorophosphate (IFP-2, Polyset); bis(4-t-butylphenyl) iodonium tetraphenylborate (IPB,

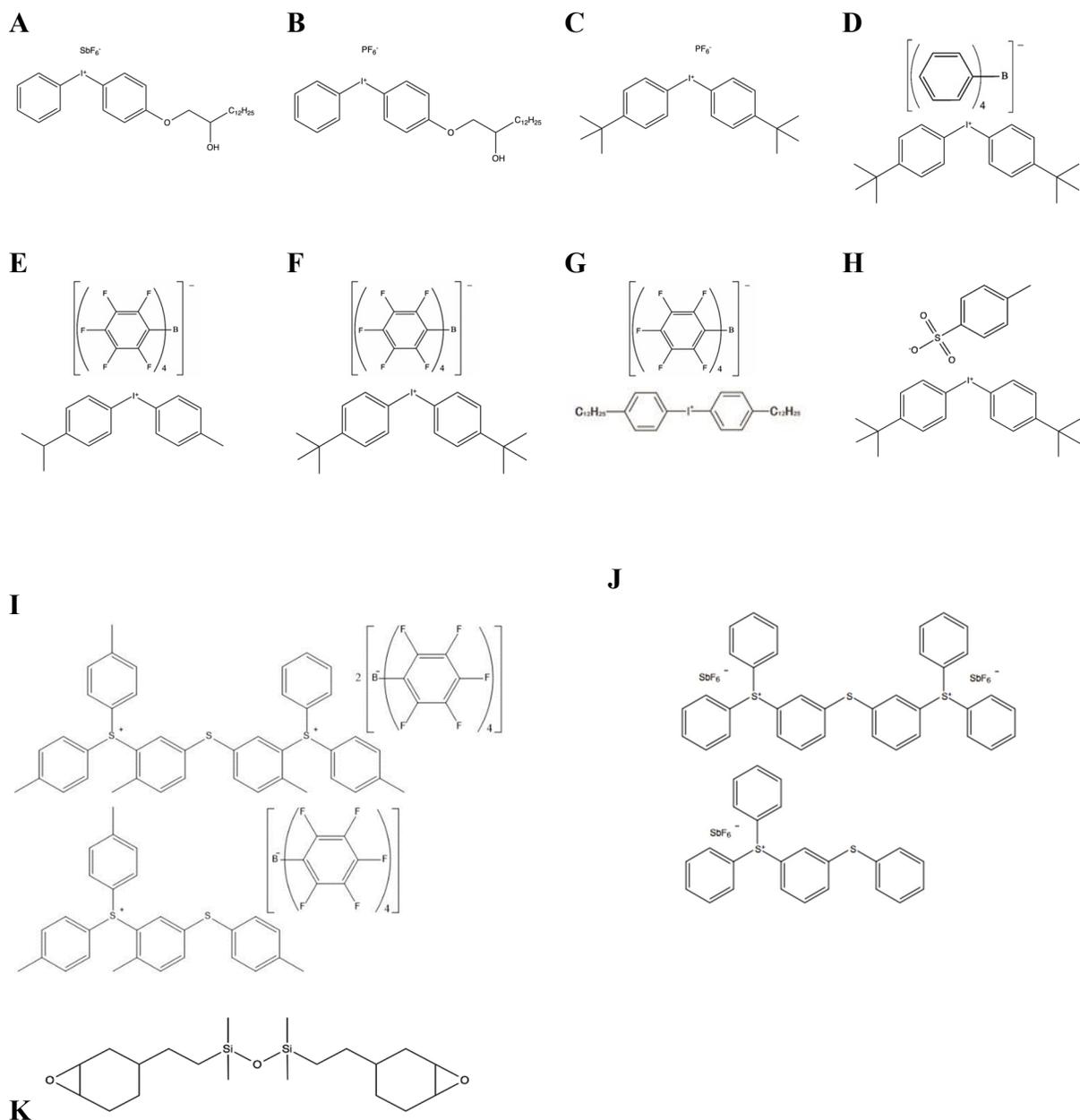


Figure 1. Chemical structures of the onium salts used in this study: IFA (A), IFP (B), IPB (C), IFP-2 (D), IFPB (E), IFPB-2 (F), IFPB-3 (G), ITS (H), SFPB (I), and SFA (J), as well as the epoxide monomer EDS (K).

Polyset); 4-isopropyl-4'-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate (IFPB, Polyset); bis(4-t-butylphenyl) iodonium pentafluorophenylborate (IFPB-2, Tronly); diaryliodonium pentafluorophenylborate (IFPB-3, Tronly); bis(4-t-butylphenyl) iodonium tosylate (ITS, Polyset); triarylsulfonium pentafluorophenylborate salts, mixed (SFPB, Tronly); and triarylsulfonium hexafluoroantimonate salts, mixed (SFA, Tronly). Although many of the same cations and anions are repeated, they are paired in different combinations. In addition, the impact of photoinitiator structure on

kinetics and conversion was determined by reacting each photoinitiator with the epoxide monomer 1,3-bis(2-(7-oxabicyclo[4.1.0]heptan-3-yl)ethyl)-1,1,3,3-tetramethyldisiloxane (EDS, Polyset). All materials were used as received.

Methods

UV-Vis Spectroscopy

The absorbance of the onium salts and epoxide monomer was measured using an ultraviolet-visible (UV-Vis) spectrophotometer (Cary 50 UV-Vis Spectrophotometer, Varian Inc.). Samples were prepared at 0.1, 0.01, and 0.001 wt% in the solvent acetonitrile, which was chosen to minimize absorbance overlap. The Beer-Lambert Law (Equation 1) was used to calculate the molar absorptivity of each onium salt:⁴

$$A = \varepsilon c l \quad (1)$$

where A is absorbance measured by the spectrophotometer, ε is molar absorptivity, c is molar concentration, and l is path length (1 cm here). Absorbance data from the UV-Vis spectra were used to calculate ε as a function of wavelength for each concentration, and then an average ε was calculated for each monomer and onium salt and plotted versus wavelength.

The emission of a mercury arc lamp (Acticure® Ultraviolet/Visible Spot Cure system, EXFO Photonic Solutions Inc.) fitted with a 250 – 450 nm filter, was measured using a fiber-optic spectrometer (USB 4000, Ocean Optics). The relative overlap of onium salt absorbance and lamp emission was calculated using Equation 2:

$$L = c \int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda)E(\lambda) d\lambda \quad (2)$$

where λ is the wavelength, L represents relative overlap, and E is the relative intensity of the lamp output as a function of wavelength. Only when both absorbance and emission are large is a significant amount of energy absorbed by the onium salt.

Real-time Raman spectroscopy

Equivalent-overlap formulations of each onium salt in the epoxide monomer EDS were prepared using 0.5 wt% IFA in monomer as a reference (*i.e.*, the concentration of onium salt for each formulation was chosen to have the same relative overlap (L) as 0.5 wt% IFA). Formulations were injected into quartz capillary tubes with 1 mm ID, and the samples were then illuminated with an average power of 580 mW/cm² using the mercury arc lamp. Raman spectra were collected during 4 minutes of illumination (light cure) and an additional 8 minutes after illumination (dark cure) using a holographic probe head (Mark II, Kaiser Optical Systems Inc.) with a single-mode excitation fiber delivering approximately 220 mW from a 785-nm near-infrared laser to the samples. Spectra were collected with 1 s exposure time and 3 accumulations.

Monomer conversion to polymer was calculated from the Raman spectra of each formulation (Figure 2) as follows:

$$\text{Fractional Conversion} = 1 - \frac{I(t)_{rxn}/I(t)_{ref}}{I(0)_{rxn}/I(0)_{ref}} \quad (3)$$

where peak heights (I) were measured prior to illumination ($t = 0$) and during light and dark cure (t) for both the epoxide reaction (rxn) peak at 787 cm^{-1} and the stable reference (ref) peak at 1447 cm^{-1} .⁵

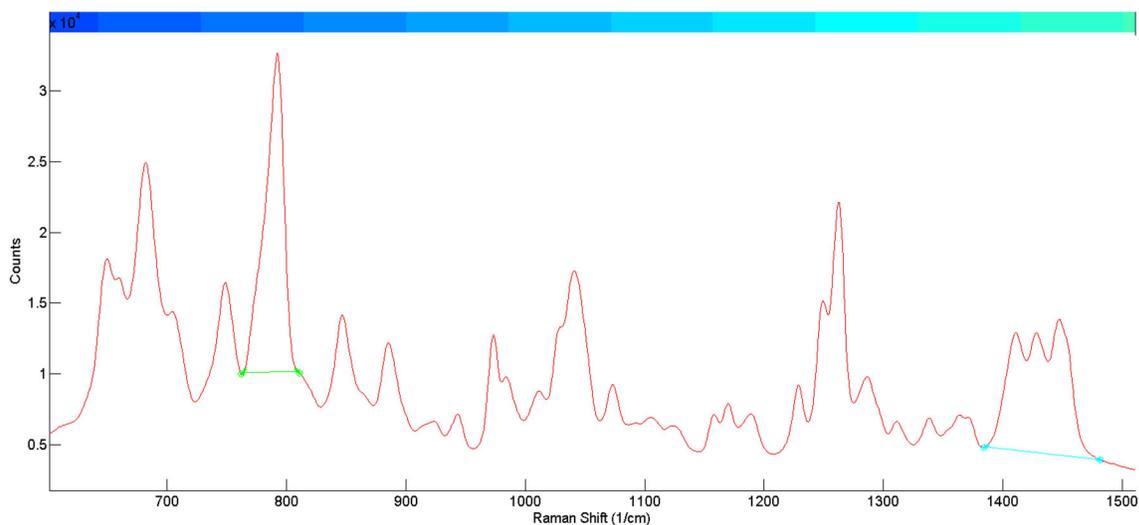


Figure 2. Raman spectrum of the epoxide monomer EDS. The reaction peak at 787 cm^{-1} and the reference peak at 1447 cm^{-1} were used to determine monomer conversions.

Results and Discussion

Key absorbance data, such as maximum measured ϵ , were obtained from UV-Vis spectra collected for each onium salt in acetonitrile (Table 1). The sulfonium salts (last two table entries) have much higher maximum measured ϵ , up to 5.6 times higher, than the iodonium salts. They also absorb as high as 360 nm^{-1} ; whereas, the iodonium salts absorb light below 342 nm . All photoinitiators exhibited the strongest absorbance at wavelengths $\sim 250 \text{ nm}$ or below. The spectral data were truncated at 240 nm because acetonitrile absorbs light below 240 nm and obscures the absorbance profile of the onium salt; however, all the onium salts absorb light below 240 nm based on the peak profiles collected here (Figure 3) and spectra presented in the literature collected in a different solvent.⁶

Representative absorbance spectra for four iodonium salts are shown in Figure 3. The shapes of the absorbance profiles for onium salts with the same iodonium cation are nearly identical (*i.e.*, compare IFA with IFP and IFPB with ITS); however, all four onium salts have different counterions. These results confirm that the anion has very little effect on the light absorbance of the onium salt. Compared to the iodonium salts, the sulfonium salts absorb light much more strongly over a wider range of wavelength (note the difference in the y-axis scales of the two graphs in Figure 3). The increased absorbance is due to the greater number of aromatic rings in the sulfonium salts: more conjugated double bonds result in increased light absorbance.

Table 1. Absorbance data for each onium salt with ϵ calculated in acetonitrile using Beer's Law.

Onium Salt	Maximum measured ϵ (L M ⁻¹ cm ⁻¹)	Wavelength at max ϵ (nm)	Range of absorbance (nm)
IFA	13,800	251	240 – 342
IFP	16,100	250	240 – 340
IFP-2	23,200	241	240 – 310
IFPB	20,100	240	240 – 315
IFPB-2	22,900	240	240 – 330
IFPB-3	18,800	240	240 – 330
IPB	31,800	240	240 – 306
ITS	20,800	241	240 – 310
SFA	51,400	240	240 – 360
SFPB	77,100	240	240 – 356

In order for the onium salts to initiate polymerization, they must absorb sufficient energy from an appropriate light source. Therefore, the absorbance spectra of the onium salts were compared to the emission spectrum of the mercury arc lamp (Figure 4). The lamp emission is highest above 360 nm, with the most intense peaks centered around 365, 405, and 440 nm. Neither SFA nor IFA overlap well with the output of the lamp, and the only significant light absorbance for the iodonium salts is from the small UV-C peak ~250 nm. Although these photons have comparatively high energies, this mismatch between onium salt absorbance and lamp emission explains the need for effective photosensitizers and/or deep-UV LEDs.

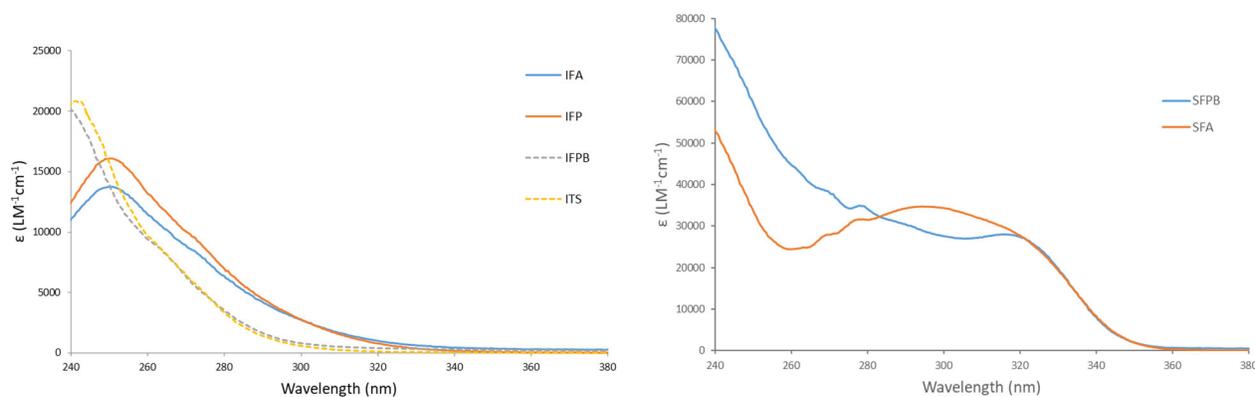


Figure 3. Molar absorptivity of four iodonium (left) and two sulfonium (right) salts: ϵ was calculated in acetonitrile using Beer's Law.

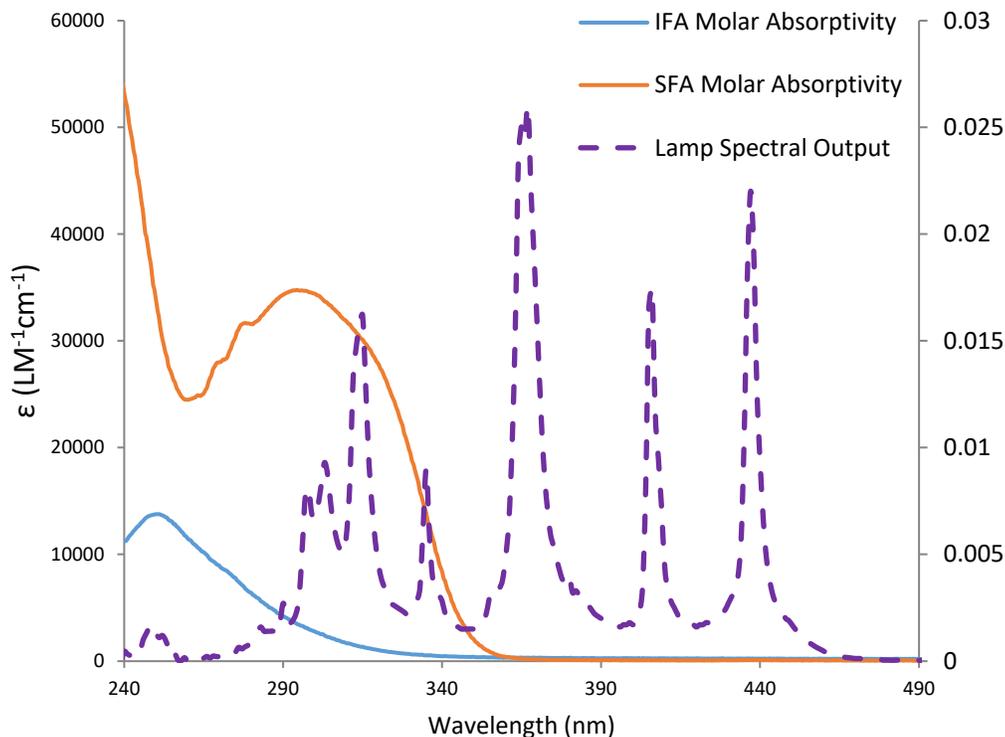


Figure 4. Identification of spectral overlap between the emission of the mercury arc lamp and the absorbance of representative onium salts (IFA and SFA).

The relative overlap (L) with the mercury arc lamp was calculated for each onium salt using Equation 2 (Figure 5). The sulfonium salts have approximately a 10-fold greater overlap with the lamp compared to the iodonium salts. Thus, the concentration of sulfonium salts required to absorb energy and initiate polymerization should be much lower than for the iodonium salts.

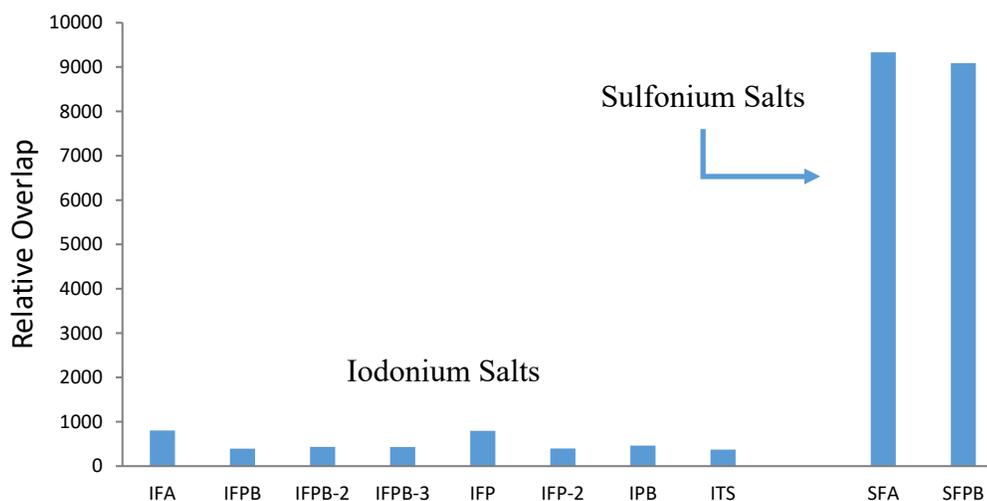


Figure 5. Relative overlap (L) of each onium salt absorbance with the lamp emission: sulfonium salts (right) have a 10-fold higher overlap than the iodonium salts (left).

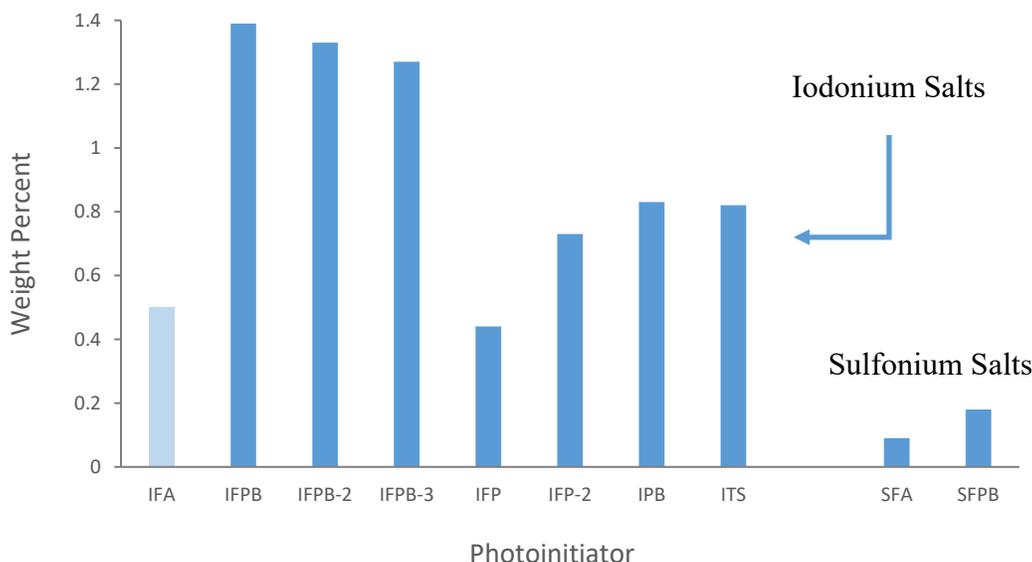


Figure 6. Weight percent of onium salt required for equivalent overlap (L) using 0.5 wt% IFA in the epoxide monomer EDS as the reference.

Onium salt concentrations needed for equivalent light absorbance were calculated for equivalent-overlap solutions of each onium salt in EDS using 0.5 wt% IFA as the reference solution (Figure 6). For example, a solution of 0.8 wt% IPB would absorb the same amount of light as a solution of only 0.1 wt% SFA. As expected from the results of Figure 5, the concentrations of sulfonium salt needed to absorb an equivalent amount of light are much lower (up to 15 times less) than the concentrations of iodonium salts.

The equivalent-overlap solutions were then illuminated using the mercury arc lamp, and the conversion of EDS was calculated for each. However, only solutions of IFA, IFPB, IFPB-2, IFPB-3, and SFPB had measurable conversion (Figure 7). For these cationic photoinitiators with pentafluorophenylborate and hexafluoroantimonate counterions, ~50% conversion was achieved, except in the case of IFPB-2, which reached ~60% conversion. The uniformity of these outcomes suggests that an equal amount of light absorbance results in the same amount of conversion, regardless of the photoinitiator used.

On the other hand, solutions of IFP, IFP-2, IPB, ITS, and SFA did not initiate polymerization. This lack of reaction is because the counterions formed weaker acids that were not strong enough to protonate the oxygen atom in the epoxide ring in order to create the cationic active center.⁴ IFP and IFB both have the hexafluorophosphate counterion, which is similar in structure with the hexafluoroantimonate counterion that successfully initiated polymerization with IFA. Antimonate is a much larger atom than phosphorous (it is two periods below phosphorous on the periodic table); therefore, it is more polarizable and better able to stabilize its negative charge. As a result of its larger size, the antimonate counterion more readily gives up the positively charged acidic proton, making it more acidic. IFP-2 has the phenylborate counterion, which is similar in structure to the pentafluorophenylborate counterions found in IFPB, IFPB-2, and IFPB-3 – all of which initiated polymerization. The electronegative fluorine atoms present in pentafluorophenylborate (but absent in phenylborate) help stabilize the negative charge on the borate atom, allowing the acid to give up the

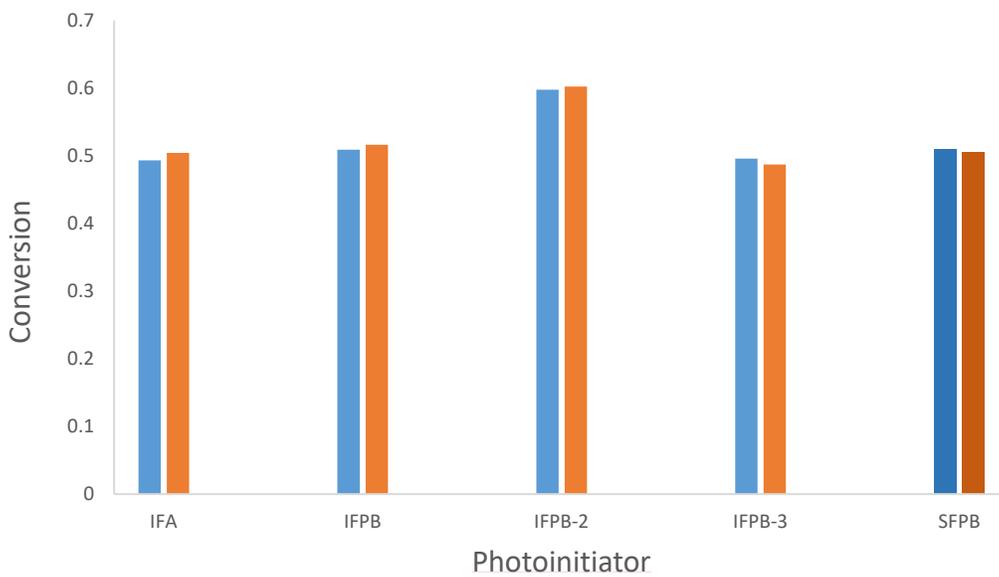


Figure 7. Fractional conversion of the epoxide monomer EDS for solutions containing equivalent-overlap concentrations of the cationic photoinitiators. Conversions for both trials were calculated from real-time Raman spectroscopic data.

hydrogen ion more easily and again making it a stronger acid. Finally, ITS has a tosylate counterion, which is not nearly as strong an acid as the other counterions. The sulfur atom is even smaller and less polarizable than the phosphorous atom in hexafluorophosphate, and the oxygen atoms surrounding it are fewer and less electronegative than the fluorine atoms. Thus, it is even less able to stabilize the negative charge (though resonance of the sulfur-oxygen double bonds helps). Curiously, SFA also did not initiate polymerization, even though it has the hexafluoroantimonate counterion, which is a very strong acid and has been demonstrated to be effective with IFA. It is not clear why SFA did not lead to any conversion. However, SFA did have the highest amount of overlap with the mercury arc lamp and therefore the lowest concentration for an equivalent-overlap solution (*i.e.*, 0.09 wt%). It is possible that this concentration was simply too low to initiate polymerization and that a threshold concentration of SFA is required before measurable polymerization occurs.

Using the real-time conversion data (Figure 8), the rate of photopolymerization can be estimated for the equivalent-overlap photoinitiator solutions. Though approximately the same conversion was achieved with all five photoinitiators that initiated polymerization, IFA was the slowest to reach that final conversion. The shallower initial slope of the IFA curve relative to the SFPB and IFPB-2 curves indicates that less conversion is achieved over the same time period. Thus, the fluoroantimonate counterion (in IFA) resulted in an initial polymerization rate that is less than a third the rate exhibited by the pentafluorophenylborate counterion (in SFPB and IFPB-2). When in solution, the negatively charged counterion and positively charged active center form a stable ion pair. The closer the counterion is to the active center, the more stable the ion pair is. When the active center is stabilized, it is less reactive.⁷ Therefore, the system reacts more quickly with the large and bulky pentafluorophenylborate counterion. The hexafluoroantimonate counterion is relatively much smaller than the pentafluorophenylborate counterion and can get closer to the active center, stabilizing it and reducing the rate at which it reacts.

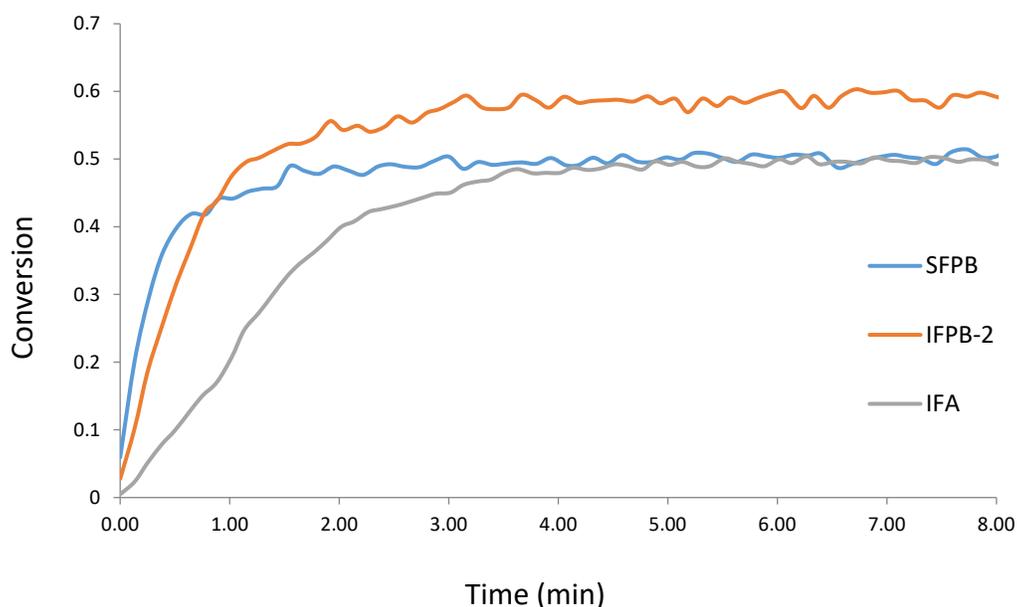


Figure 8. Conversion profiles of the epoxide monomer EDS for three cationic photoinitiators of equal-overlap concentration. The rate of polymerization is directly proportional to the slope of the conversion profiles, with steeper slopes indicating a faster rate. Conversions were calculated from real-time Raman spectroscopic data.

Conclusions

Onium salts have provided the means for successful implementation of cationic photopolymerization. Their effectiveness relies both on the absorbance characteristics of the cation and the reactivity of the anion. In this work, eight iodonium and two sulfonium salts were compared on an equal-absorbance basis. With an extra aryl ring bonded to the central atom, salts with sulfonium cations absorbed significantly more light over a broader range of wavelengths than salts with iodonium cations. Neither type of onium salt had a substantial overlap with the emission of a mercury arc lamp; however, with an absorbance spectrum that extends into the UV-A, the sulfonium salts had a relative overlap that was an order of magnitude greater than that of the iodonium salts. This enhanced overlap translated into significantly smaller amounts of sulfonium salt needed in equal-overlap solutions with the epoxide monomer than their iodonium salt counterparts. When these equal-overlap solutions were illuminated, iodonium salts with pentaphenylborate, hexafluorophosphate, and tosylate counterions did not result in measurable polymerization because these counterions do not form strong enough superacids to initiate the reaction. The sulfonium salt with the hexafluoroantimonate counterion also did not initiate polymerization; however, this inactivity was most likely due to its extremely low concentration in the equal-overlap solution series. Otherwise, pentafluorophenylborate and hexafluoroantimonate were the best-performing anions, and equal-overlap solutions with these anions achieved approximately the same final conversion, underscoring the direct relationship between energy absorbed and conversion. Although final conversions were similar, photoinitiators with the pentafluorophenylborate counterion resulted in polymerization rates two times faster than the photoinitiator with the hexafluoroantimonate counterion. This rate difference is due to counterion size: the larger pentafluorophenylborate counterion cannot associate as closely with the cationic active center to stabilize it, thereby rendering it less reactive. The results of this systematic study with onium salts provides guidelines to compare cationic

photoinitiator performance on a normalized basis, so that structure and concentration can be selected based on lamp availability and reactivity requirements.

Acknowledgements

This material is based upon work supported by the Iowa Center for Research by Undergraduates. We would like to thank 3M and Hampford Research Inc. for their generous donation of materials.

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