Design and Synthesis of Photoacid Generating Systems

James V. Crivello

Department of Chemistry and Chemical Biology
Rensselaer Polytechnic Institute
Troy, New York, 12180 U.S.A.
crivej@rpi.edu

The development of highly efficient onium salt-based photoacid generating systems has provided many new opportunities for the design of novel photocuring and imaging systems. This communication focuses on some of the more recent efforts in designing and synthesizing efficient photoacid generating systems with tailored wavelength response. The use of these photoacid generating systems in a number of applications is described.

Keywords: photacid generation, onium salts, diaryliodonium salts, triarylsulfonium salts, photopolymerization, photoimaging

1. Introduction

Prior to the early 1970s the only practical types of photopolymerizations that could be carried out were based on free-radical and photoinduced condensation reactions. Both of these types of photopolymerizations were employed for the photocuring of coatings and as negative photoresists in imaging systems. The key discovery of onium salts in our laboratory as latent photochemical sources of strong Brønsted acids opened the way to conduct cationic photopolymerizations and paved the way for their use in photocurable coatings, printing inks, adhesives as well as many other applications. It also enabled the now ubiquitous use of these photoacid generators in both positive and negative working microelectronic photoresists. An attempt will be made in this communication to briefly outline some of the most prominent past and current advances in this field and to discuss prospects for future developments.

Diaryliodonium **I** and triarylsulfonium salts **II** with the general structures depicted below were the first practical photoacid generators discovered and are still widely employed in both academic research and for commercial uses. These two classes of onium salts are highly photosensitive with quantum yields that range from 0.5–0.9 [1,2]. The mechanism by which the photolysis of these onium salts occurs has been thoroughly investigated [3,4]. Scheme 1 depicts a

highly simplified mechanism for the photolysis of diaryliodonium salts. Triarylsulfonium salts undergo photolysis by a very similar mechanism.

Scheme 1

Absorption of light in the UV region of the spectrum leads to excitation of the diaryliodonium salt that is followed by both homolytic and heterolytic cleavage of a carbon-iodine bond (eq. 1). This takes place by both an in and out of cage processes. Several highly reactive species are generated including: cations, radicals and cation-radicals. Depending on the specific application, one can utilize these species

to conduct free radical and/or cationic processes. In the presence of proton donor donors that may consist of solvents, monomers or trace impurities, the highly reactive cationic species react further to generate protonic acids (eq. 2). By choice of the appropriate anion, MtX_n^- , of a diaryliodonium or triarylsulfonium salt, one can photochemically generate acids whose strengths can varied from relatively weak carboxylic acids to extremely powerful superacids such as $HSbF_6$ or HPF_6 . Onium salts that photolytically generate the latter superacids are both necessary and useful for conducting vinyl and ring-opening cationic polymerizations. For this reason, such onium salts are widely employed in high performance negative working epoxy-novolac photoresists, in stereolithography and for a wide variety of UV-curing applications. When onium salts are used in positive microlithographic photoresists where their function is to provide acids for catalytic photodeblocking reactions, anions such as perfluoroalkylsulfonates are usually employed.

2. Modification of Diaryliodonium and Triarylsulfonium Salt Photoacid Generators

Over the course of the past 30 years, literally, hundreds of different onium salts have been purposefully synthesized to meet the specific requirements of photocuring and photoimaging applications. Among the first modifications carried out on onium salts were to improve their solubility characteristics in non-polar monomers and polymer matrices. This was achieved by preparing unsymmetrical diaryliodonium [5] and triarylsulfonium salts [6] bearing alkyl or alkoxy substituents. Shown in eqs. 3 and 4 are two straightforward synthetic routes that were used for the preparation of these compounds.

Unsymmetrical onium salts with the above structures are crystalline compounds, yet they readily dissolve in virtually all monomers examined. It was observed that such onium salts showed little tendency to segregate in photoresists during spin casting and

this was found to be critical for the production of vertical sidewalls and eliminating residue during development.

An especially challenging task was to design and develop an onium salt photoacid generator that could be used together with epoxy-silicone release agents. Diaryliodonium salt **III** bearing two highly branched dodecyl groups was expressly developed for that purpose [7]. Photocrosslinkable silicone release coatings are currently applied and photocured on paper and plastic at high rates of speed using **III** without the use of volatile organic solvents and with the consumption of only a fraction of the energy previously required for thermal cure. In recent years, this technology has revolutionized the pressure sensitive adhesive industry.

Due to their unique combination of excellent photosensitivity and thermal stability, in recent years triarylsulfonium salts have been the focus of much synthetic development. A number of studies of these photoacid generators were carried out to determine the effects of structure on the absorption characteristics, photosensitivity and the ability of onium salts to function as photoacid generators. These investigations employed well-established methods for the synthesis of these compounds as well as several novel preparative methods. For example, the copper catalyzed arylation of the three isomeric (o, m and p) disulfides **IV** was carried out using diphenyliodonium salts as depicted in eq. 5 to give quantitative yields of **V**.

While all three isomeric sulfonium salts represented by **V**, were good photoacid generators, the 4-thiophenoxy-substituted compound displayed outstanding photosensitivity when broad spectrum UV irradiation was used. Only this isomer possessed a

strong absorption band at 305 nm in addition to the bands at 225 nm that are usually displayed by simple triphenylsulfonium salts. The observed higher reactivity is a result of the improved long wavelength spectral absorption due to the presence of the thiophenoxy chromophor in the 4-substituted isomer. This was demonstrated in two ways as shown in eqs. 6 and 7. Removal of the 4-thiophenoxy chromophor by arylation to give the bisulfonium salt, **VI**, that possesses only the short wavelength band at 225 nm. At the same time, sulfonium salt **VII** prepared as shown in eq. 7 bearing two thiophenoxyphenyl groups possesses both the long and short wavelength absorption bands. The band at 305 nm in **VII** has twice the molar absorption as the S(4-thiophenoxy)-S,S-diphenylsulfonium salt **V**. Accordingly, **VII** displays the highest level of photosensitivity that we have yet observed for a triarylsulfonium salt.

Another series of triarylsulfonium salt photoacid generators, **VIII**, containing the thianthrenium ion was prepared using the synthetic route depicted in eq. 8. The desired sulfonium salts are obtained in excellent yields by the condensation of thianthrene-S-oxide with aromatic compounds containing electron-donating **R** groups using a mixture of P_2O_5 and methanesulfonic acid (MSA). Thianthrenium salts, **VIII**, display excellent photosensitivity while at the same time are very thermally stable. The solubility and crystalline characteristics of these photoacid generators may be readily modified by varying the substituent, **R**.

2. Photosensitization of Onium Salts

Due to the presence of the aryl groups, diaryliodonium and triarylsulfonium photoacid generators absorb strongly in the short wavelength region of the ultraviolet spectrum. This makes them especially attractive for microlithographic photoresists. Originally developed for use in I-line positive photoresists, onium salt photoacid generators have been employed in each successive generation of photoresists until the present time. It now appears that they will remain important in optical lithography well into the ultra short wavelength UV regime.

At the same time, the recent development of efficient, long wavelength UV and visible emitting light sources such as lasers and LEDs for imaging, printing, graphic arts, stereolithography and medical and dental applications has created an increasing demand for photopolymers with sensitivities in the 400–500 nm spectral region. Accordingly, there has been a continuing effort in this laboratory to develop practical onium salt-based photoacid generating systems with the required long wavelength sensitivity. Attempts to appreciably spectrally broaden the sensitivity of triarylsulfonium salts solely through structural modification have met with only limited success. As noted above, specialized triarylsulfonium salts have been synthesized with UV absorption maxima from 305 to 309 nm [8,9]. However, attempts to further extend the sensitivity of this class of compounds to longer wavelengths by direct structural modification in this laboratory have largely failed.

Fortunately, one of the most attractive features of onium salts is the ability to broaden their spectral sensitivity through the use of electron-transfer photosensitization. Scheme 2 shows the proposed mechanism for the photosensitization of triarylsulfonium salts. Analogous mechanisms can be written for the photosensitization of diaryliodonium salts.

Scheme 2.

Electron-transfer photosensitization is, in essence, a photoinduced redox process that involves first, the absorption of light by the photosensitizer, **PS**, to give the corresponding excited species **[PS]*** (eq. 9). An excited state complex (exciplex) is often formed as an intermediate between the onium salt and the excited photosensitizer (eq. 10). Subsequently, the onium salt is reduced by a formal one electron-transfer between the two reaction partners (eq. 11) yielding a triarylsulfur free radical and the photosensitizer cation-radical. The rapid decomposition of the resulting unstable triarylsulfur free radical (eq. 12) prevents back electron-transfer and renders the overall process essentially irreversible. The photosensitizer cation-radical can decay by a number of pathways, usually generating a Brønsted acid (eq. 13). It should be noted that during electron-transfer photosensitization, both the onium salt and the photosensitizer are irreversibly consumed. Due to their lower reduction potentials, diaryliodonium salts are more easily photosensitized by an electron-transfer process than triarylsulfonium salts [10].

A wide variety of compounds have been found to function as photosensitizers for onium salt photoacid generators. Among these are low molar mass carbazoles [11], phenothiazines [12] and polymers containing these moieties. Typically, these compounds are active photosensitizers at wavelengths below 380 nm. Common polynuclear aromatic hydrocarbons such as pyrene and perylene can serve as electron-transfer photosensitizers for both diaryliodonium and triarylsulfonium salts at wavelengths from 380 to 500 nm [13,14]. However, these compounds have the drawback that they are significantly toxic. Recently [15], we have reported that the three benzophenothiazine isomers, **IXa-c**, shown below are efficient photosensitizers for triarylsulfonium salts at wavelengths above 400 nm.

An example is shown in Fig. 1 in which the crosslinking photopolymerization of limonene dioxide is carried out in the presence and absence of **IXb**. An optical filter was used to limit the UV light only to wavelengths greater than 400 nm. In the absence of

IXb no polymerization was observed, whereas with the photosensitizer present, rapid, exothermic polymerization ensues.

Figure 1. Study of the photosensitized polymerization of limonene dioxide using 1.0 mol% S(4-n-decyloxyphenyl)-S,S-diphenylsulfonium hexafluoro-antimonate and 0.5 mol% 12H-benzo[b]phenothiazine (**IXb**) (light intensity 20 mW/cm²).

During the past year, [16], we have reported the surprising discovery that the inexpensive and nontoxic naturally occurring plant dye, curcumin, **X**, is a potent photosensitizer for diaryliodonium salt photoacid generators at wavelengths from 300 to 500 nm. Curcumin is a bright yellow compound that is isolated from the common spice, turmeric, used in Southeast Asia to make curry. It is often used as a coloring agent for various foods including mustard. It is especially efficient as an electron-transfer photosensitizer for visible light irradiation and has been used together with epoxidized vegetable oils to make and solar cure fiber-reinforced composites. As with all electron-transfer photosensitizers, curcumin is oxidized during irradiation in the presence of diaryliodonium salts. Upon prolonged irradiation, the dye undergoes almost complete bleaching.

We are especially optimistic about the future of this latter technology. Work conducted in this laboratory suggests that using dyes like curcumin together with

monomers produced from biomass, it will be possible for even unskilled people to produce and fabricate a wide variety of composite items for everyday use by simple, direct exposure to rays of the sun. At the same time, the technology is environmentally attractive, non-polluting and easy to implement.

3. Conclusions

The development of diaryliodonium and triarylsulfonium salt photoacid generators has afforded many new opportunities for their use not only in

imaging and photolithographic processes. Current intense research activity in this area suggests that onium salts will be a continued focus of the effort to develop ever more sensitive photoresists with higher resolution capabilities. At the same time, onium salts are finding applications in many new fields including; coatings, adhesives, printing inks as well as in many aspects of nanotechnology. Considerable progress has also been made in developing photosensitizers to address emerging applications that require sensitivity in the long wavelength UV and visible regions.

References

1. J.V. Crivello, *Ring-Opening Polymerization* D.J. Brunelle, editor, Hanser, Munich, (1993) p. 157.
2. C. Selvaraju, A. Sivakumar and P. Ramamurthy *J. Photochem. Photobiol. A: Chem.*, **138** (2001) 213.
3. J.L. Decktar and N.P. Hacker *J. Chem. Soc. Chem. Commun.* (1987) 1592.
4. R.J. DeVoe, M.R.V. Sahyun, N. Serpone and D.K. Sharma *Can. J. Chem.* **65** (1987) 2342.
5. J.V. Crivello and J.L. Lee *J. Polym. Sci. Part A: Polym. Chem.* **27** (1989) 3951.
6. S.R. Akhtar, J.V. Crivello and J.L. Lee *J. Org. Chem.* **55** (1990) 4222.
7. R.P. Eckberg and R. W. LaRochelle, *U.S. Patents* 4,279,717, July 21, 1981; 4,421,904, Dec. 20, 1983.
8. J.V. Crivello and J.H.W. Lam, *J. Polym. Sci. Part A: Polym. Chem.* **18** (1980) 2677.
9. J.V. Crivello, J. Ma and F. Jiang, *J. Polym. Sci. Part A: Polym. Chem.* **40**(20) (2002) 3465.
10. J.V. Crivello, *UV Curing Science and Technology*; S.P. Pappas, editor, Technology Marketing Corp., Stamford, CN, (1978) p. 24.
11. J.V. Crivello, *Photoinitiated Polymerization*, *ACS Symposium Series 847*, K.D. Belfield and J.V. Crivello, editors, ACS, Washington, D.C. (2003) p. 219.
12. Z. Gomurashvili and J.V. Crivello, *J. Polym. Sci. Part A: Polym. Chem.* **39**(8) (2001) 1187.
13. Reference 8 p. 53.
14. J.V. Crivello and J.H.W. Lam *J. Polym. Sci. Part A: Polym. Chem.* **17** (1979) 1059.
15. J.V. Crivello, *J. Polym. Sci. Part A: Polym. Chem.* (paper in press)
16. J.V. Crivello and U. Bulut *J. Polym. Sci. Part A: Polym. Chem.* **43** (2005) 5217.