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Cationic Polymerization: New Developments and Applications

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Summary: The chemistry and technology of photoinitiated cationic polymerization is a rapidly advancing field of investigation. This article reports on recent developments made in our laboratory in the development of new photoinitiators and photosensitizers. S,S-Dialkyl-S-phenacylsulfonium salts have been prepared using a new, highly efficient and cost-effective synthetic method and their use in the polymerization of various monomer systems studied. Also described is the development of alkoxyanthracene photosensitizers that may be employed to broaden the spectral sensitivity of various onium salt photoinitiators including the new S,S-dialkyl-S-phenacylsulfonium salts. A marked acceleration of the rate of the ring-opening polymerization of epoxide monomers was achieved using these photosensitizers. This article concludes with a brief discussion of the use of photoinitiated cationic polymerizations in such typical applications as can coatings, silicone release coatings and in stereolithography.

Keywords: cationic photoinitiators; cationic photopolymerization; epoxide monomers; photosensitizers; ring-opening polymerization

Introduction

For many years, work in this laboratory has centered about exploring various methods of inducing the addition polymerization of a monomer in response to a specific trigger or stimulus. Besides presenting an interesting scientific challenge, stimuli-responsive polymerizations are highly useful processes. For example, the simple application of heat is often used to carry out thermosetting polymerization reactions employed in structural adhesives. Although widely employed, heat is a non-specific, energy wasteful means of stimulating polymerizations. The focus of our work has been to use various higher forms of radiation including light, e-beam, γ-rays, microwaves and ultrasound as well as electrolytic means of inducing polymerizations in a more controlled manner. In contrast to heat, these forms of energy can be directed by

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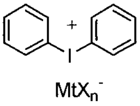
magnets, wave guides, lens, mirrors, gratings and prisms in such a manner that only the monomer or portions of the monomer under investigation are targeted and undergo polymerization. Each method of triggering polymerizations has its own characteristic advantages and disadvantages. This article will focus on recent advances made in our laboratory involving use of light as a stimulus to carry out cationic polymerizations.

Our attention has centered mainly on photoinitiated cationic polymerizations for several reasons. First, the corresponding free radical photopolymerization chemistry is well developed. At the same time, the less developed cationic photopolymerizations offer both an intellectual challenge as well as attractive mechanical and chemical properties not easily attained by free radical systems. For this reason, industrial interest and use of cationic photopolymerizations has been increasing.[1] Today, photoinitiated cationic polymerizations are not only being employed for coating and printing ink applications where the high speed and solvent-free use has been the main driving force in their development, but also in such applications as stereo- and photolithography where the high photosensitivity, excellent adhesion and mechanical properties are the crucial factors in their adoption.

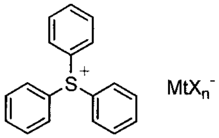
Results and Discussion

Photoinitiators

Previously, we have reported the discovery that diaryliodonium (**I**) and triarylsulfonium salts (**II**) are highly efficient photoinitiators of cationic polymerization.[2]



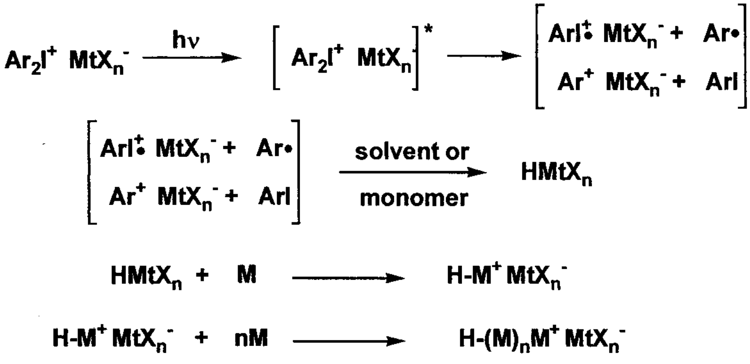
I



II

These latter compounds are so called "cleavage photoinitiators" on the basis of the mechanism of their photolysis and initiation of polymerization. As depicted in Scheme 1 for diaryliodonium salts, photolysis of these compounds results in the irreversible cleavage of a carbon-iodine bond.

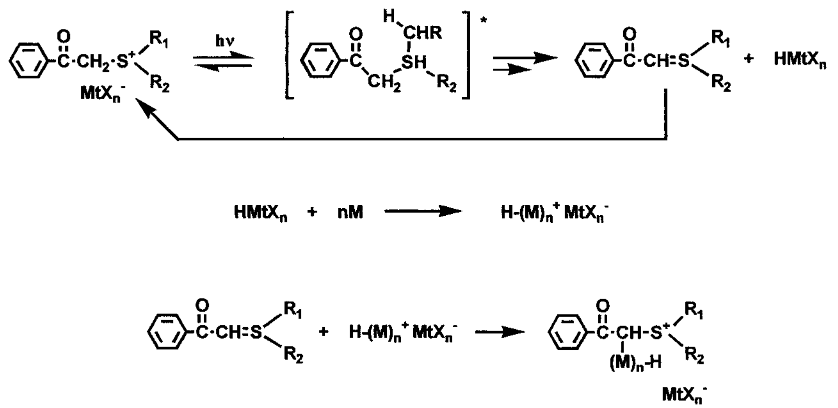
Scheme 1



The photolysis of iodonium and sulfonium salt cleavage photoinitiators is highly efficient with quantum yields ranging from 0.6-0.9.[3] A variety of reactive species are formed during photolysis including radicals, cations and cation-radicals. In subsequent steps involving reaction of the cationic fragments of the photoinitiator with the monomer, water or other protonic impurities, a Brønsted acid is generated that is derived from the anion of the starting onium salt. Accordingly, a wide range of both weak and strong acids can be photogenerated by the photolysis of diaryliodonium and triarylsulfonium salts. However, only the strongest acids are effective initiators of cationic polymerization. Particularly effective are "super acids" such as HBF_4, HPF_6, $HAsF_6$, $HSbF_6$ and $HB(C_6F_5)_4$ with Hammett acidities more negative than –15. Onium salt photoinitiators bearing the corresponding anions are capable of initiating the polymerizations of all known types of cationically polymerizable monomers.

In contrast to the above described cleavage photoinitiators, S,S-dialkyl-S-phenacylsulfonium salts as shown in Scheme 2 undergo photolysis by a markedly different mechanism.[4,5] The photolysis of this class of sulfonium salts results in excitation of the aryl ketone portion of the molecule with rapid intersystem crossing from the excited singlet to the excited triplet state. The diradical character of the photoexcited triplet carbonyl group enables this latter species to abstract a hydrogen atom from a nearby carbon atom via a six-membered ring transition state. This pathway closely resembles the well-known Norrish type II reaction mechanism.[6] Progressing by a number of subsequent electron and proton transfer steps, an ylide together with protonic acid are formed. A quantum yield for photolysis of S,S-dialkyl-S-phenacylsulfonium salts was found to be 0.43.[4] Further investigation of the mechanism showed that when the photolysis of the sulfonium salts is carried out in an inert solvent, the ylide and protonic acid recombine via a dark process to regenerate the starting sulfonium salt. However, when the photolysis of a S,S-dialkyl-S-phenacylsulfonium salt is carried out in the presence of a suitable monomer, polymerization takes place readily. An example is given in Figure 1.

Scheme 2



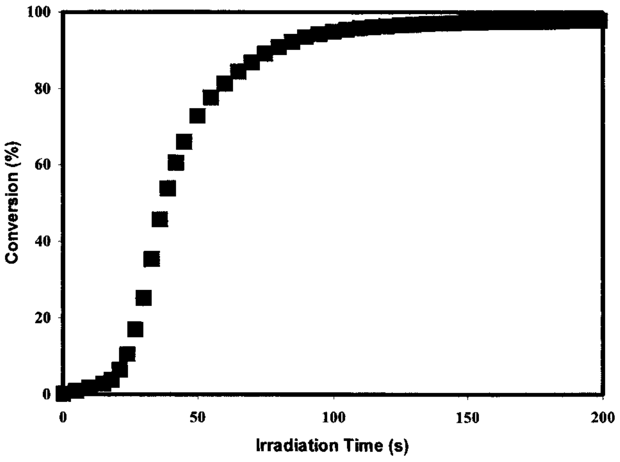
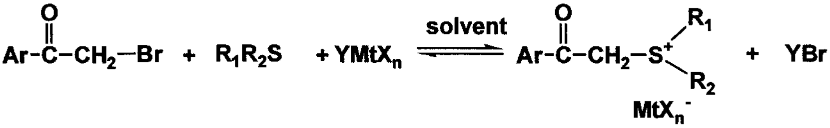


Figure 1. Photoinitiated polymerization of 2-chloroethyl vinyl ether using 0.5 mol% S-n-decyl-S-methyl-S-phenacylsulfonium SbF_6^-. (light intensity 250 mJ/cm^2 min).

Despite their excellent photosensitivity and efficiency as photoinitiators, S,S-dialkyl-S-phenacylsulfonium salts have received little commercial or academic attention. The reasons for this are several, but are chiefly related to the limitations of the synthetic method for these photoinitiators that restricts their preparation to only those compounds that are highly crystalline. Unfortunately, such photoinitiators have poor solubility in all but the most polar monomers. Recently, we[7] have discovered a simple, straightforward means of preparing these compounds that is highly versatile and provides these photoinitiators in high yields. This new method is depicted in equation shown below.



$$\mathrm{Ar{-}C({=}O){-}CH_2{-}Br} + R_1R_2S + YMtX_n \overset{\text{solvent}}{\rightleftharpoons} \mathrm{Ar{-}C({=}O){-}CH_2{-}S^{+}R_1R_2}\ MtX_n^{-} + YBr$$

A phenacyl halide is combined with a dialkyl sulfide in the presence of an alkali or alkaline earth salt of the desired anion. The desired S,S-dialkyl-S-phenacylsulfonium salt is formed directly with the driving force for the reaction provided by the formation and precipitation of an insoluble inorganic halide salt. Using this new synthetic strategy, each of the components can be varied at will. Of particular interest is the synthesis of lipophilic photoinitiators bearing long chain alkyl groups of uneven length. Such photoinitiators can be employed to polymerize very nonpolar monomers such as long alkyl chain vinyl ethers, epoxy-functional silicones and 1,2-epoxyalkanes. An example is given in Figure 2.

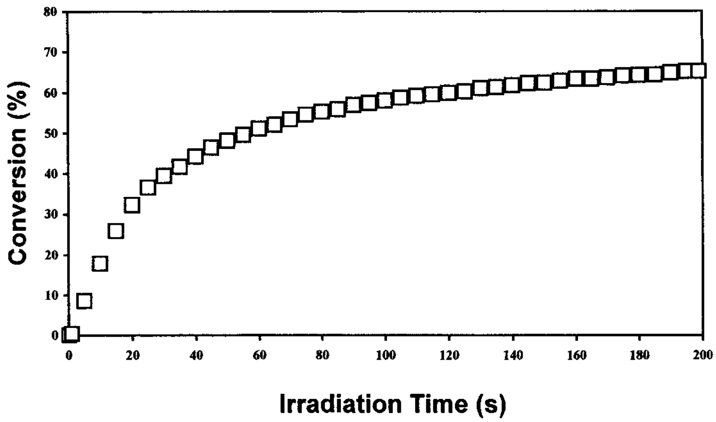
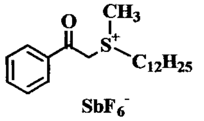
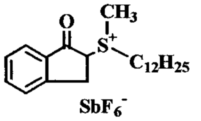


Figure 2. Photopolymerization of 1,2-epoxydecane using 1.0 wt% S,S-di-n-tetradecyl-S-phenacylsulfonium SbF_6 (light intensity 1800 mJ/cm^2 min).

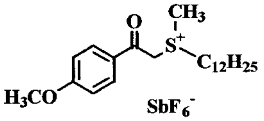
Similarly, the arylketone portion of the molecule can also be modified within wide tolerances.[8] Shown in Figure 3 are the UV spectra of three different S,S-dialkyl-S-phenacylsulfonium salts, **III-V**. The simple phenyl substituted photoinitiator has a λ_{max} at 251 nm (ε = 14000) while the inclusion of a 4-methoxy group provides a 37 nm shift to longer wavelengths (λ_{max}. 288 nm, ε = 20000). The third photoinitiator shown in this figure incorporates an indanone group in the structure (λ_{max}. 254 nm, ε = 12000). This photoinitiator was purposefully designed with the objective of improving the efficiency of the photolysis reaction by facilitating the formation of the six-membered ring transition state depicted in Scheme 2.



III



IV



V

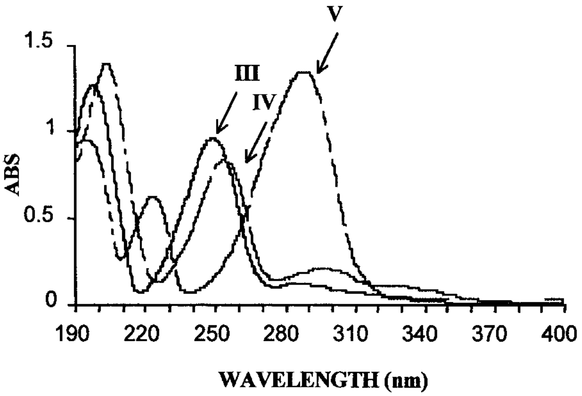


Figure 3. UV spectra of photoinitiators III, IV and V in methanol.

Figure 4 shows the results of a comparison of the three photoinitiators at the same molar concentration in the polymerization of 4-vinyl-1,2-cyclohexene dioxide. Irradiation was performed using light with wavelengths longer than 300 nm. The efficiency of the three photoinitiators is strongly related to their UV absorption characteristics. The longer the wavelength of the principle absorption band, the greater the efficiency of the photoinitiator. Thus, the 4-methoxy substituted photoinitiator shows the highest response followed by the photoinitiator that incorporates the indanone chromophor.

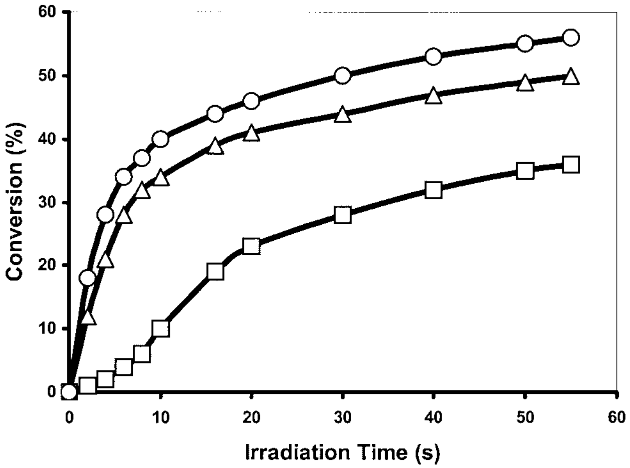


Figure 4. Photoinitiated cationic polymerization of PC-1000 using 1.0 mol % photoinitiators **III**, (□);**IV**, (Δ) and **V**, (O). (light intensity 840 mJ/cm^2 min).

Photosensitizers

Figure 5 shows the UV absorption spectra of two typical onium salt photoinitiators superimposed onto the emission spectrum of a common medium pressure mercury arc lamp. Mercury arc lamps are the most prevalent and efficient sources of UV irradiation. It is very evident that there is a considerable mismatch in these spectra and that a great deal of the output energy of the lamp is wasted since it cannot be absorbed by these photoinitiators.

It has been the goal of this research group to seek methods by which the spectral sensitivity of onium salt cationic photoinitiators can be broadened. It is anticipated if this can be achieved, that the overall efficiency of the photoinitiation process can be increased. In addition, there is an increasing use of monochromatic and narrow band light sources such as lasers and LEDs in reprographic applications. The ability to tailor the response of the photoinitiator to these light sources is essential to success in these applications. Among the most promising methods of achieving these goals is the use of photosensitization. Previously, it has been demonstrated that electron-transfer photosensitization is very effective means of broadening the spectral sensitivity of triarylsulfonium and diaryliodonium salts into the long wavelength UV and visible regions of the spectrum.[9,10] Briefly, electron-transfer photosensitization of onium salts takes place as shown in Scheme 3.

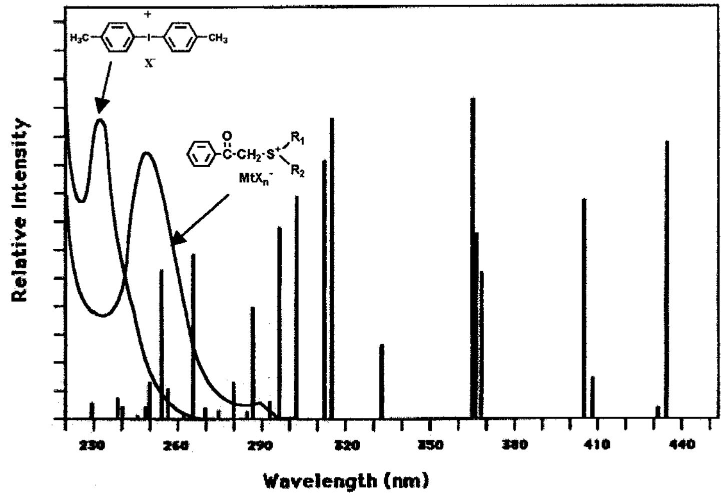


Figure 5. Superposition of the line emission spectrum of a medium pressure mercury arc lamp and the UV absorption spectra of diaryliodonium and S,S-dialkyl-S-phenacylsulfonium salts.

Scheme 3

$$\mathrm{PS} \xrightarrow{h\nu} [\mathrm{PS}]^*$$

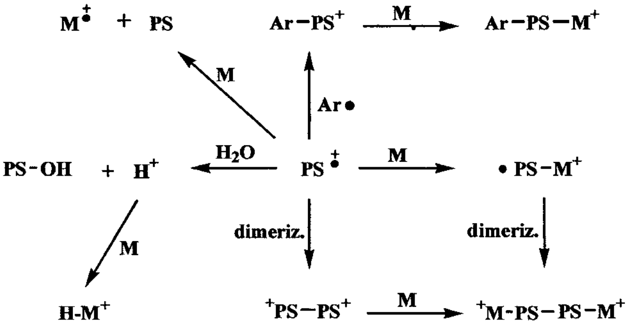
$$[\mathrm{PS}]^* + \mathrm{Ar_2I^+}\,\mathrm{X^-} \longrightarrow \underset{\textbf{exciplex}}{[\mathrm{PS} \cdots \mathrm{Ar_2I^+}\,\mathrm{X^-}]^*}$$

$$[\mathrm{PS} \cdots \mathrm{Ar_2I^+}\,\mathrm{X^-}]^* \longrightarrow [\mathrm{PS}]^{+\bullet}\,\mathrm{X^-} + \mathrm{Ar_2I}\bullet$$

$$\mathrm{Ar_2I}\bullet \longrightarrow \mathrm{ArI} + \mathrm{Ar}\bullet$$

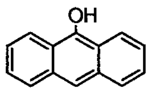
In the first step, light is absorbed by the photosensitizer, PS, and the excited photosensitizer interacts directly with the onium salt or by the initial formation of an exciplex. Subsequently, this species undergoes a formal electron transfer process during which the photosensitizer is oxidized and the onium salt is reduced. In a subsequent step, further irreversible decomposition of the reduced onium salt takes place that yields radical products. The photosensitizer cation-radical ($PS^{\overset{+}{\bullet}}$) generated by the above photoredox reaction initiates the polymerization of a cationically polymerizable monomer by any of several complex processes shown in Scheme 4.

Scheme 4

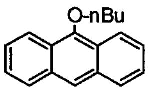


Most of the early work in this laboratory focused on the use of polynuclear aromatic hydrocarbons that display excellent long wavelength absorption characteristics and efficient electron-transfer photosensitization for all types of onium salt cationic photoinitiators. However, pyrene, anthracene and perylene are not attractive as photosensitizers due to their purported toxicity and high vapor pressure. Accordingly, alternative photosensitizers have been sought.

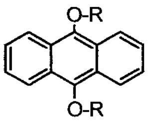
Recently, we have described a series of anthracene derivatives that resolve the above-mentioned issues and provide a high degree of photosensitization activity for essentially all onium salt cationic photoinitiators.[11] In accordance with the mechanism shown in Scheme 3, only those anthracene derivatives that possess electron-donating groups have suitably low excited state reduction potentials and are active electron-transfer photosensitizers. The preparation of several 9-mono- and 9,10-disubstituted anthracene derivatives (V-VI) were prepared by straightforward synthetic methods and the structures are shown below. Very recently, several of these same compounds have become available on a semi-commercial scale from the Kawasaki Kasei Company.[12]



VI



VI



VIIa R = n-Bu

VIIb R = n-Pr

These anthracene derivatives have their major absorption in the 200-300 nm region with a secondary, lower intensity series of absorption bands from 300-380 nm. In Figure 6 is depicted a study of the ring-opening photopolymerization of cyclohexene oxide using (4-n-decyloxyphenyl)diphenylsulfonium SbF_6^- as the photoinitiator and with equivalent amounts of various anthracene derivatives as photosensitizers. A study in which no photosensitizer was used is included for comparison.

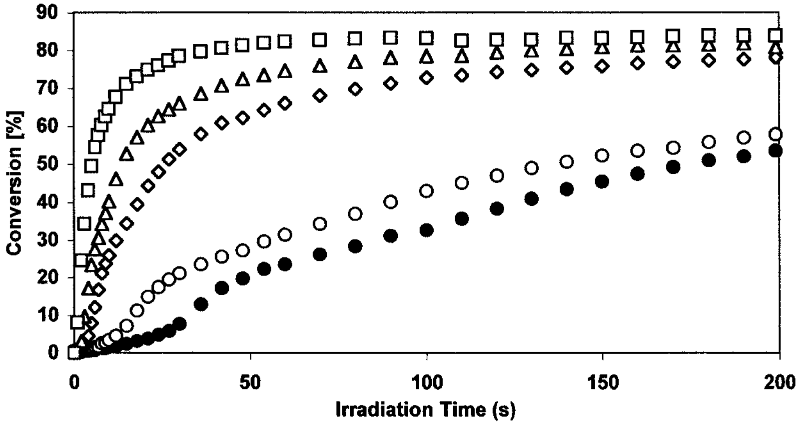


Figure 6. Photosensitized polymerization of cyclohexene oxide in the presence of 1 mol% (4-n-decyloxyphenyl)diphenylsulfonium SbF_6^- in the presence of 1 mol% of various anthracene derivatives. 9,10-di-n-butoxyanthracene, (□); 9-butoxyanthracene, (△); anthracene, (◇); anthrone, (○); no photosensitizer; (●); light intensity 310 mJ/cm^2 min.

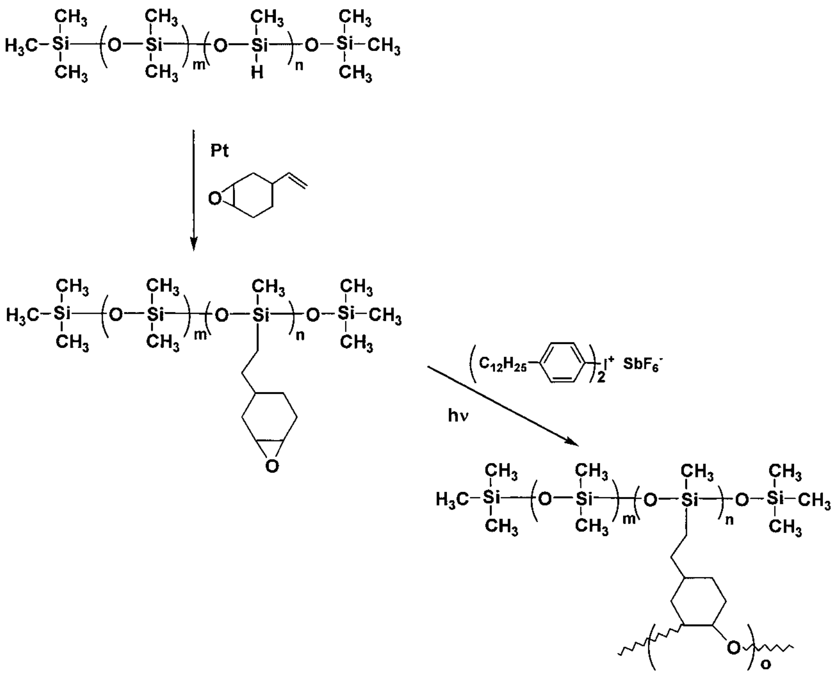
Only anthracene derivatives bearing electron-donating groups are electron-transfer photosensitizers for onium salts. These groups increase the electron density within the excited aromatic nucleus facilitating its oxidation by the removal of an electron by the onium salt photoinitiator. Anthrone is only slightly better than anthracene as a photosensitizer for triarylsulfonium salts. The equilibrium between anthrone and its anthrole tautomer is 89:11. Thus, anthrone displays little characteristic anthracene absorption in the > 300 nm region. In contrast, mono- and dialkoxysubstituted anthracenes display excellent ability to photosensitize not only the photolysis diaryliodonium salt photoinitiators but also triarylsulfonium and S,S-dialkyl-S-phenacylsulfonium salt photoinitiators as well.

Applications of Photoinitiated Cationic Polymerization

The current applications of photoinitiated cationic polymerization are many and varied. Generally speaking, these applications fall into two broad classifications; commodity uses such as coatings, adhesives and printing inks and high performance uses, for example, photolithography, stereolithography, holographic data storage and optical wave-guides. Only a few typical examples of these applications will be given here.

One of the first large scale applications of the cationic ring-opening photopolymerization of epoxides was the innovative use of UV curable graphic inks and overprint varnishes employed by the Coors Brewing Company. The Coors Brewing Company is the fourth largest beer brewing company in the U.S. The UV can coating process was carried out on a continuous basis at a rate of approximately 2000 cans per minute with a total production of 4 billion cans per year. Another very large coating application involves the application and UV cure of silicone release coatings. These silicone-based coatings are applied onto various substrate backings to permit the transfer of pressure sensitive adhesive coated labels, tabs, etc. The chemistry of the synthesis silicone-epoxide oligomers is used in this application is depicted in Scheme 5.[13,14] Silicone oligomers bearing multiple Si-H functionality along the polymer backbone are subjected to a platinum catalyzed hydrosilation with 4-vinyl-1,2-epoxide to provide oligomers with pendant epoxide groups. These materials are then combined with a lipophilic diaryliodonium salt photoinitiator such as di(4-dodecylphenyl)iodonium SbF_6^- [15,16] and then irradiated with UV light to provide a low surface energy crosslinked silicone release coating. The cure of these solventless coatings occurs very rapidly and continuous rates of production of 300-450 m/min are routine. This chemistry is now widespread and is employed by the General Electric Corporation, Rhone-Poulenc and by Goldschmidt.

Scheme 5



Stereolithography is a technique for creating three-dimensional solid objects using photopolymerizations.[17,18] The apparatus for this process is depicted in Figure 7. A computer generated three-dimensional object is mathematically divided into thin slices approximately 3-5 mils (75 - 125 mm) in thickness. Each slice is then drawn by a computer driven laser onto the surface of a liquid photopolymer. Polymerization occurs rapidly as the drawing process takes place resulting in a solid, polymeric reproduction of the slice. The first slice is flooded with the liquid photopolymer and the second slice is drawn onto the top surface of the first one. This process is repeated until the entire solid object is built up. Stereolithography provides engineers and designers with rapid prototypes of their designs and greatly increases the productivity and speed with which complex items as automobiles and aircraft can be built. This technique also has many other potential applications including custom tailored prosthetics and medical implants. Most of the photopolymers employed in stereolithography today incorporate resins and monomers that are based on photoinitiated cationic crosslinking polymerizations.[19,20] This is due to the outstanding mechanical properties of the epoxy resins that are used along with their low toxicity. The photosensitivity, optical density, monomer reactivity and overall shrinkage are the critical factors of the photopolymer which must be carefully controlled to enable the construction of three dimensional objects which are faithful to the original design.

As stereolithography undergoes further expansion into still other applications such as mold making and is used to produce actual functional parts, increasing demands are being placed on the mechanical properties of the resulting photopolymers. This will provide an opportunity for additional research into the design of novel cationically polymerizable monomer and oligomer systems.

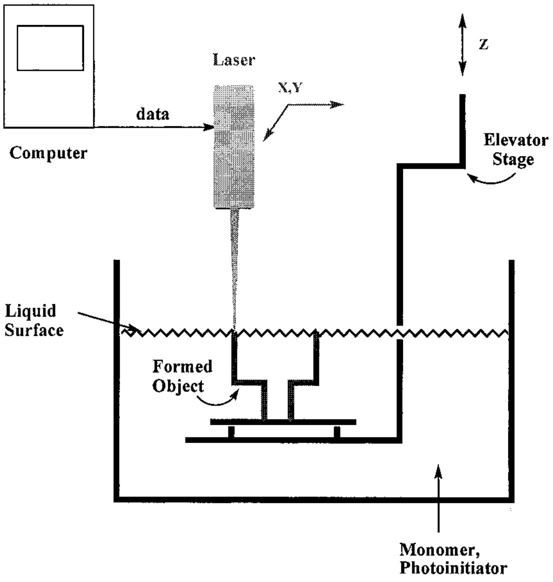


Figure 7. Apparatus for carrying out stereolithography.

Conclusions

In this article, we have demonstrated that the research area of photoinitiated cationic polymerizations is still in its infancy and is undergoing rapid development both with respect to activity in basic research and in the development of new applications. Herein, we have discussed our recent results in the design and synthesis of new cationic photoinitiators and photosensitizers. Similarly, a considerable effort is being directed towards the synthesis of novel cationically polymerizable monomer and oligomers. All of this activity is being impelled by the demands being placed on this technology by emerging applications.

Acknowledgements

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