Macromol. Symp. **2004**, *215*, 165-177

Advances in the Design of Photoinitiators, Photo-Sensitizers and Monomers for Photoinitiated Cationic Polymerization

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Summary: The present article reports on recent work from this laboratory that has led to advances in several areas of the field of photoinitiated cationic polymerization. Two different classes of novel photoinitiators 5-arylthianthrenium salts and 4-hydroxyphenyl dialkylsulfonium salts have been prepared and their use in the polymerization of various monomer systems studied. Also described is the development of both monomeric and polymeric photosensitizers that may be employed to broaden the spectral sensitivity of various onium salt photoinitiators. Acceleration of rate of the ring-opening polymerization of epoxide monomers has been achieved through the use of benzyl alcohols. Further, benzyl alcohols bearing sensitizing groups were found to be especially interesting as combination accelerators-photosensitizers. Lastly, epoxy monomers having groups with easily abstractable protons display exceptional reactivity in photoinitiated ring-opening cationic polymerization. A mechanism has been proposed to explain this observation.

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

Introduction

Both academic and industrial interest in cationic photopolymerizations has been increasing as the number of commercial applications of this chemistry has multiplied and as the economic and environmental advantages of this technology have become apparent.[1] Today, photoinitiated cationic polymerizations are not only being employed for coating and printing ink applications where the high speed and solvent-free use had been the main driving force in their development, but also in such applications as stereo- and photolithography where the high photosensitivity and excellent mechanical properties are the crucial factors in their adoption. As the

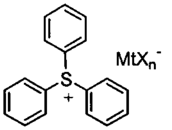
DOI: 10.1002/masy.200451114

interest in these photosensitive systems moves to ever-higher performance applications, there is an increasing interest in the development of advanced systems with better performance characteristics. Accordingly, in this laboratory, we have pursued efforts to prepare novel, more photosensitive photoinitiators, improve their spectral absorption characteristics through photosensitization, increase the rates of polymerization of monomers through the use of accelerators and attempt to prepare new monomers through rational design. In this article, we will report on the results we have recently obtained in each of these fields.

Results and Discussion

Photoinitiators

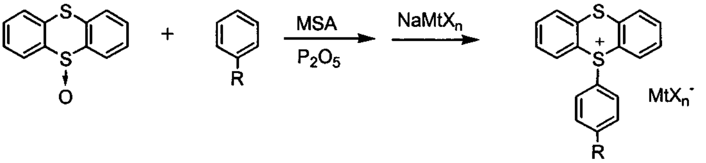
Among the best cationic photoinitiators yet developed are triarylsulfonium salts. These compounds combine a unique set of almost paradoxical properties. Triarylsulfonium salts display excellent photosensitivity with quantum yields estimated in the range of 0.6-0.9.[2] At the same time, these photoinitiators are extraordinarily thermally stable. This allows even highly reactive monomers to be processed at temperatures approaching 150 °C without inducing spontaneous thermal polymerization. It has, however, been noted that the major region of photosensitivity of simple triarylsulfonium salts such as **I** ($MtX_n^- = BF_4^-, PF_6^-, AsF_6^-, SbF_6^-$, etc.) lies in the short wavelength region of the UV spectrum.[3]



I

Increasingly, there is need to carry out photoinitiated cationic polymerizations using long wavelength UV and visible radiation. For example, many new imaging systems are being developed that employ either lasers or light emitting diodes as monochromatic or narrow band irradiation sources. Typically, these efficient light sources emit light in the long wavelength UV and visible regions. Lastly, there is considerable present interest in developing visible wavelength responsive photoinitiator systems that can be used to conduct photopolymerizations with solar irradiation. To address such applications, it is necessary to design photoinitiators that have photoactive absorption bands at specific, predetermined wavelengths. With this rationale in mind, work in this laboratory has been exploring the development of synthetic methods for the preparation of novel photoinitiators.

5-Arylthianthrenium salts with absorption in the mid (300-400 nm) range of the UV spectrum have been prepared as shown in equation 1 by the direct condensation of thianthrene-5-oxide in the presence of methanesulfonic acid (MSA) and phosphorous pentoxide.[4] This method is particularly attractive for the synthesis of 5-arylthianthrenium salts bearing electron-donating substitutents, R. A large number of these compounds were prepared with different counterions of low nucleophilicity and then examined as photoinitiators for a variety of vinyl and ring-opening cationic polymerizations.



II eq. 1

Figures 1 and 2 respectively, show the photopolymerizations of vinyl ether and epoxy monomers. These studies demonstrate that 5-arylthianthrenium salts are excellent photoinitiators for these two types of cationically polymerizable monomers.

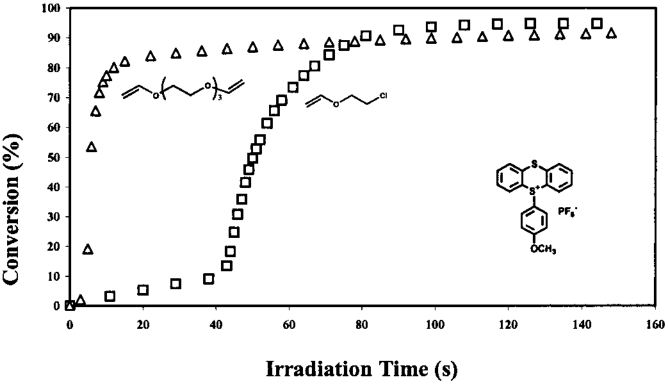


Figure 1. Comparison of the photopolymerizations of 2-chloroethyl vinyl ether and triethyleneglycol divinyl ether (DVE-3) carried out in the presence of 0.5 mol% of 5(4-methoxyphenyl)thianthrenium SbF_6^-. (light intensity 206 mJ/cm^2)

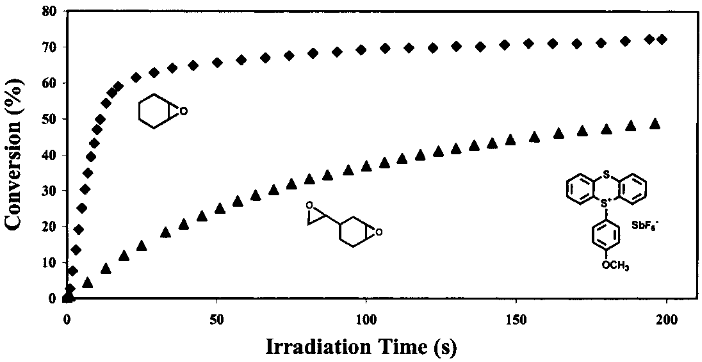
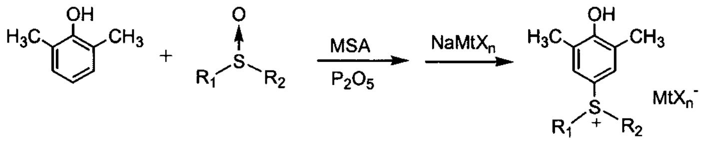


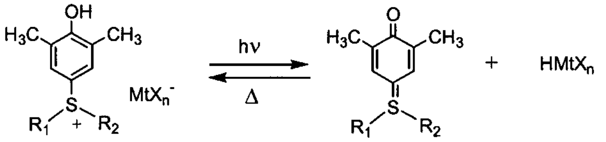
Figure 2. Study of the photopolymerization of cyclohexene oxide and 4-vinylcyclohexene dioxide carried out in the presence of 0.5 mol% of 5(4-methoxyphenyl)thianthrenium SbF_6^-. (light intensity 128 mJ/cm^2)

The synthetic method described above in equation 1 has also been effectively applied to the synthesis of another class of sulfonium salt cationic photoinitiators. 4-Hydroxyphenyl dialkylsulfonium salts, **III**, can be prepared by the reaction of appropriately substituted phenols with dialkylsulfoxides as shown in equation 2.[5]



III eq. 2

In a similar fashion, a series of 2-hydroxyphenyl dialkylsulfonium salts can be prepared starting with 2,4-disubstituted phenols as substrates. Using this method, it is possible to prepare sulfonium salts with alkyl groups, R_1 and R_2 of any desired chain length. Such photoinitiators can be designed to be soluble even in quite nonpolar, lipophilic monomers. Whereas the photolysis of 5-arylthianthrenium and other triarylsulfonium salts proceeds by a mechanism in which the substrate undergoes the irreversible cleavage of a carbon-sulfur bond, the photolysis of 4- and 2-hydroxyphenyl dialkylsulfonium salts takes place by a reversible mechanism.[6] This mechanism is depicted in equation 3 for a typical member of this class of photoinitiators.



IV eq. 3

During photolysis, the photoexcited sulfonium salt releases the acid, $HMtX_n$, and simultaneously generates the corresponding ylide, **IV**. Upon cessation of the irradiation, ylide and acid recombine to regenerate the starting sulfonium salt. This reversibility can be readily observed when hydroxyphenyl dialkylsulfonium salts such as **III** are used as photoinitiators.

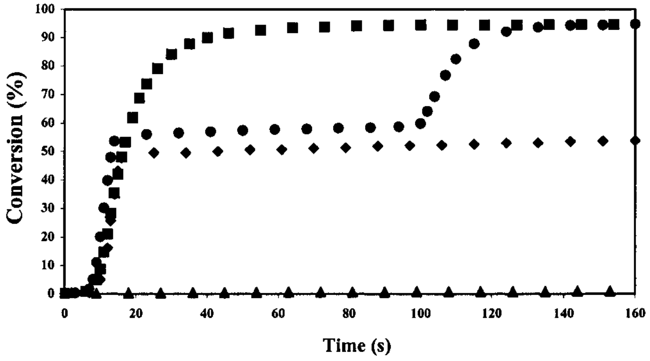


Figure 3. Study of the photopolymerization of 2-chloroethyl vinyl ether carried out in the presence of 1.0 mol% of 4-hydroxy-3,5-dimethylphenyl 1-n-decyl methyl sulfonium hexafluorophosphate. (▲) irradiation for 5 seconds; (■) continuous irradiation; (◆) 15 seconds irradiation and (●)15 seconds irradiation followed by 85 seconds dark and then continued irradiation (light intensity 850 mJ/cm^2)

Figure 3 shows an investigation of the photopolymerization of 2-chloroethyl vinyl ether under various irradiation conditions. As can be noted in Fig. 3, continuous irradiation with UV light results in the rapid consumption of the monomer. The photopolymerization exhibits a 10 second inhibition period during which trace impurities in the system react with the acid that is photochemically generated. If irradiation is conducted for a time shorter than the induction period, essentially no polymerization is observed. On the other hand, irradiation for fifteen seconds results in approximately a 50% consumption of the monomer. Once the shutter is closed, the polymerization essentially stops. Repeating this latter experiment and allowing the polymerization to stand in the dark for 85 seconds followed by continuing the irradiation results in immediate resumption of the polymerization. These results strongly support the reversibility of the photolysis mechanism.

Photosensitizers

The development of novel synthetic methods for the preparation of onium salt cationic photoinitiators has provided photoinitiators with a high degree of photosensitivity in the mid- to short wavelength UV. Progress towards the development of photosensitive cationic systems that are responsive at long UV wavelengths has been achieved through the use of photosensitization. Previously it has been demonstrated that electron-transfer photosensitization is a very effective means of broadening the spectral sensitivity of sulfonium and iodonium salts into the long wavelength UV and visible regions of the spectrum.[7,8] Briefly, electron-transfer photosensitization of onium salts takes place as shown in Scheme 1.

Scheme 1

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

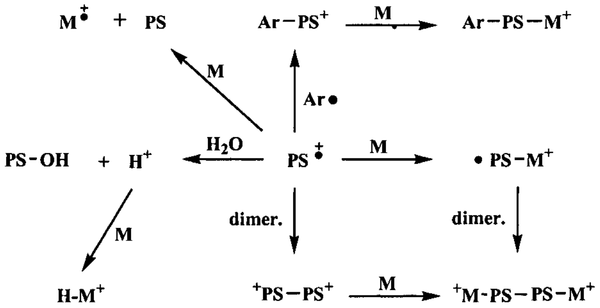
$$[\mathrm{PS}]^* + \mathrm{Ar_2I^+\,X^-} \longrightarrow \underset{\textbf{exciplex}}{[\mathrm{PS}\cdots\mathrm{Ar_2I^+\,X^-}]^*}$$

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

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

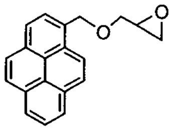
Light is first absorbed by the photosensitizer (PS) and the excited photosensitizer interacts directly with the onium salt or by the initial formation of an excited state complex. Subsequently, these species undergo a formal electron transfer in which the photosensitizer is oxidized and the onium salt is reduced. In a subsequent step, irreversible fragmentation of the diaryliodine free radical takes place to yield additional radical products. The photosensitizer cation-radical (PS$^{+\bullet}$) generated by the above photoredox reaction initiates the polymerization of a cationically polymerizable monomer by any of several complex processes shown in Scheme 2.

Scheme 2

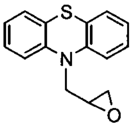


Most of the early work in this laboratory focused on the use of polynuclear aromatic hydrocarbons that display excellent long wavelength absorption characteristics and efficient electron-transfer photosensitization for all types of onium salt cationic photoinitiators. However, the disadvantage in using photosensitizers such as pyrene, anthracene and perylene is their purported toxicity. Accordingly, alternative photosensitizers have been sought.

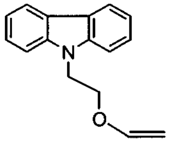
The design of photosensitizers bearing cationically polymerizable functional groups was seen as a solution to the above problem.[9,10,11] Such photosensitizers as **V-VII** shown below were prepared and shown to undergo copolymerization with either vinyl or heterocyclic compounds that polymerize by cationic ring-opening reactions as well as provide a photosensitization function.



V



VI



VII

Figure 4 depicts one such study. The inclusion of VI together with the monomer, limonene dioxide, results in the marked overall acceleration of the photopolymerization.

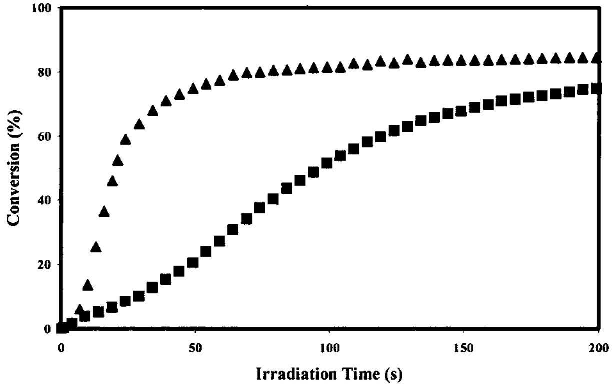


Figure 4. Comparison of the photopolymerization of limonene dioxide in the presence (▲) and absence (■) of 0.5 % of 10-(2,3 epoxypropyl)-phenothiazine), **VI**, using 1.0 % (4-n-decyloxyphenyl) diphenylsulfonium SbF_6^- as photoinitiator. (Light intensity 250 $mJ/cm^2 \cdot min$)

An interesting study of the photosensitized polymerization of limonene dioxide is shown in Figure 5. Both N-vinyl carbazole (NVK) and its polymer (PVK) display excellent photosensitization activity and to the same degree. Thus, PVK and similar types of polymers bearing pendant carbazole, anthracene, pyrene, perylene and phenothiazine groups are excellent photosensitizers for onium salt induced cationic photopolymerizations. These polymeric photosensitizers have the further benefits of being nonvolatile, nontoxic and easily handled.

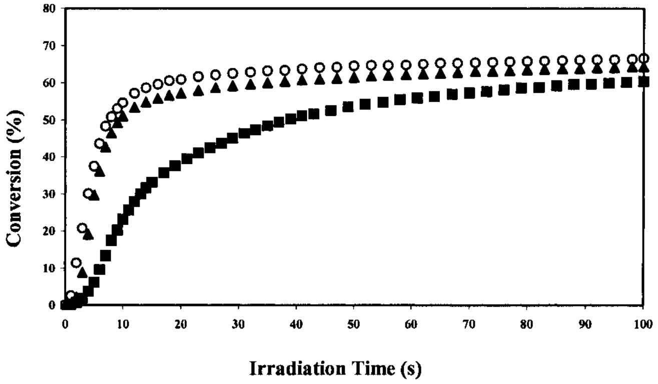


Figure 5. FT-RTIR comparison of the polymerization of limonene dioxide in the presence of 2.0% NVK (○) and PVK (▲) no photosensitizer (■). (light intensity 145 mJ/cm^2·min; 0.05% (4-n-decyloxyphenyl) diphenylsulfonium SbF$_6^-$)

Accelerators

During the course of exploring alternative means for increasing the speed of cationic ring-opening polymerizations of epoxide monomers other than photosensitization, it was observed that the addition of small amounts of benzyl alcohols markedly accelerates the rates of those polymerizations.[12] For example, in Figure 6 is depicted a study of the photoinduced polymerization of 4-vinylcyclohexene dioxide (VCHDO) in the presence of an iodonium salt and various benzylic alcohols.

Acceleration of the photopolymerization of this difunctional epoxide monomer can be attributed to two effects related to the benzyl alcohol. First, as has been demonstrated by Penczek, Kubisa and their coworkers, the addition of alcohols to the ring-opening polymerization of epoxides results in rapid transfer. Higher and more rapid conversions are generally observed for the polymerizations of such monomers since gelation is retarded. The alcohol is incorporated into the growing polymer chain as a benzyl ether end group. A second mechanism that takes place is illustrated in Scheme 3.

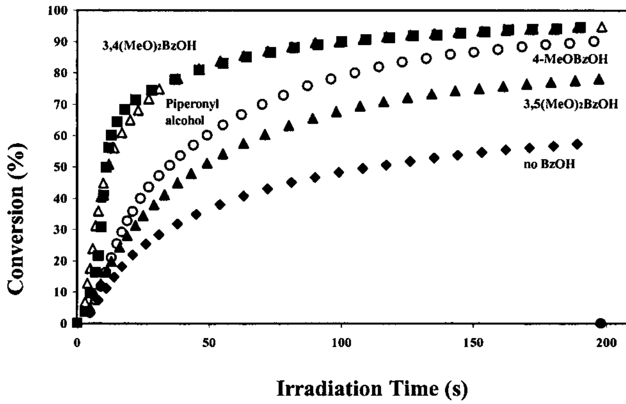
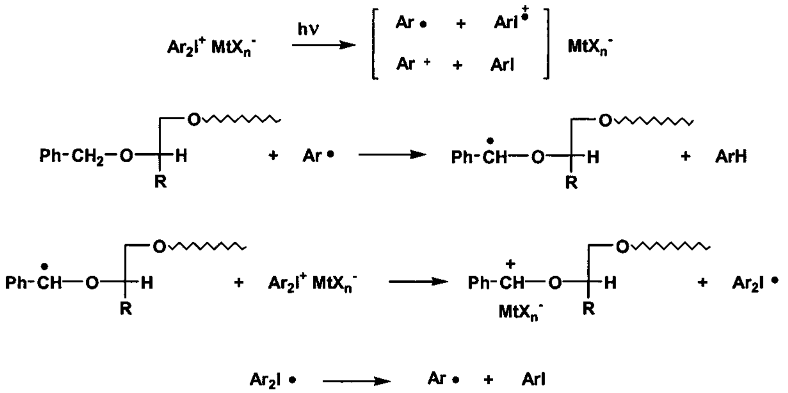


Figure 6. Comparison of the accelerating effects of various benzyl alcohols (20%) bearing electron donating groups on the cationic ring-opening photopolymerization of VCHDO. (photoinitiator, 1.0 % IOC10; light intensity 190 mJ/cm^{2}min).

Scheme 3



The photolysis of diaryliodonium salts generates a number of species among which are aryl radicals, radical cations and cations. Photopolymerization is generally attributed to the cationic species or their byproducts (i.e. protonic acids). Generally, the radical products are neglected in this process. However, when easily abstractable benzylic ether hydrogen atoms are present, they may be abstracted to form benzylic radicals that are attached to the ends of the growing polymer chains. Such radicals are readily oxidized to the corresponding benzyl cations in the presence of diaryliodonium salts. Simultaneously, the diaryliodine radical that is formed decomposes to yield an aryl radical and an aryl iodide. The aryl radical participates in a chain reaction in which the iodonium salt is consumed by a photoinitiated process that produces benzyl cations. In such a process, a large number of cationic initiating species are produced by the absorption of a few protons. This amplification effect is observed as acceleration in the rate of the polymerization of the monomer. Figure 6 also reveals that benzyl alcohols bearing electron-donating groups are most effective as accelerators. Particularly effective in this regard are 3,4-dimethoxybenzyl alcohol and piperonyl alcohol (3,4-methylenedioxybenzyl alcohol). This observation can be explained by noting that such groups stabilize both radical and cationic intermediates proposed in the mechanism of Scheme 4.

A further evolution of this concept is shown in Figure 7 in which the benzylic alcohol contains a group that can also perform a photosensitizing function. Exceedingly rapid polymerization of cyclohexene oxide is observed in the presence of 1-pyrenemethanol due to its ability to function as a photosensitizer, chain transfer agent and free radical accelerator.[13]

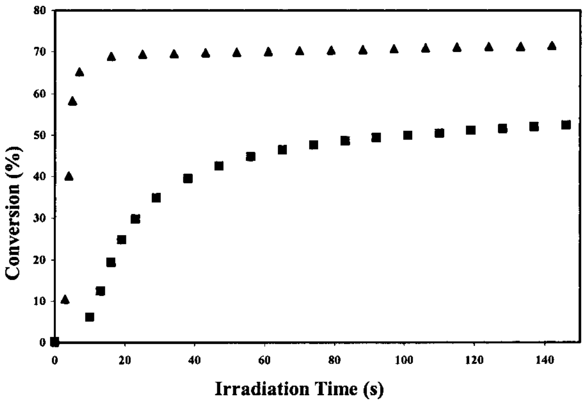
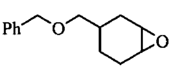


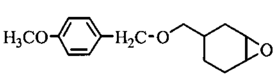
Figure 7. Kinetic study of the cationic photopolymerization of cyclohexene oxide using 0.01% IOC10 in the absence of a photosensitizer (■) and with 0.2% (▲) 3-perylenemethanol. (light intensity 178 mJ/cm^2 min)

Novel Monomers

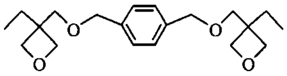
Several new monomers have been designed to take advantage of the radical induced decomposition process described in Scheme 3.[14,15] The structures of some of these monomers are depicted below.



VIII



IX



X

Each of these monomers contains a benzylic ether group to provide easily abstractable hydrogen atoms that can interact with the photoinitiator in a manner similar to that proposed in Scheme 4. In Figure 8 the photopolymerization of monomers **VIII** and **IX** is shown to be extremely rapid even under the low light intensity illumination conditions (200 mJ/cm^{2}min) used.

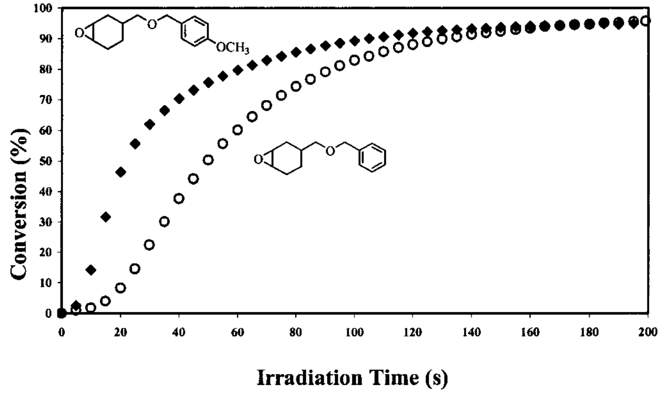


Figure 8. Comparison of the cationic photopolymerizations of **VIII**, (○) and **IX**, (◆);(photoinitiator, 1.0 % (4-n-decyloxyphenyl)phenyliodonium SbF_6^-; light intensity 200 mJ/cm^{2}min)

Conclusions

Based on the results presented in this article, it can be concluded that many aspects of photoinitiated cationic polymerizations can be manipulated to achieve desired results. The photosensitivity and spectral response of these systems can be adjusted through the synthesis of novel photoinitiators and photosensitizers. The rates of cationic photopolymerizations can be accelerated through the use of benzyl alcohol accelerators and by the design of monomers that incorporate abstractable hydrogen atoms.

Acknowledgements

The authors are grateful to the National Science Foundation and to the Petroleum Research Fund administered by the American Chemical Society for financial support of this research.

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