DOI: 10.1002/masy.200650801

Indian Turmeric and its Use in Cationic Photopolymerizations

James V. Crivello, Umut Bulut*

Summary: Curcumin, an intensely yellow dye isolated from Indian turmeric is an excellent electron-transfer photosensitizer for cationic vinyl and ring-opening polymerizations. Especially attractive features of curcumin are its strong absorption, broad spectral sensitivity, efficient electron-transfer, low toxicity and low cost. Using curcumin as a photosensitizer, the cationic photopolymerizations of a variety of monomers were carried out including such naturally derived monomers as epoxidized terpenes and epoxidized vegetable oils. The impact of this technology on applications such as housing, boat-building and water distribution is discussed.

Keywords: cationic photopolymerization; curcumin; epoxide ring-opening polymerization; photosensitization; turmeric

Introduction

In recognition of the increased demand, higher cost and dwindling supply of petroleum as the world-wide basic source of polymeric materials, the topic of “green polymer chemistry” has become the recent subject of many papers and symposia[1–3]. In addition, there is also a growing perception and concern that the global environment is steadily degrading as industrialization accelerates in many parts of the world and the demand for commodity plastics steadily increases. For some time, it has been obvious that ultimately, the source of feedstocks for polymers will have to shift from its current petroleum base to biorenewable substrates. The biorenewable replacement substrates will necessarily have to be commodity materials; readily available and inexpensive. Furthermore, to meet stringent cost requirements, such substrates will have to be either used as obtained or undergo minimal chemical modification. In addition, it will also be necessary to ensure that all phases of the culture, isolation and chemical modification and fabrication of the biorenewable polymers are energy-efficient, pollution-free and environmentally compatible. Gradually, we are becoming aware that to meet such requirements in the future it may be advantageous to do less rather than more synthetic polymer chemistry. It is also apparent that the only way in which this can be achieved is through the genetic engineering of plants solely for the purpose of producing either monomers or polymers.

In this laboratory, we are taking some first steps towards the realization of the above goals. Over the years, we have focused our attention on the chemistry of photoinitiated cationic polymerizations[4]. These polymerizations are inherently attractive because they are rapid and highly energy efficient. Since they may be carried out in bulk, the use of potentially environmentally damaging solvents can be avoided. Moreover, using this chemistry, the cationic photopolymerizations of a wide range of vinyl and heterocyclic monomers can be carried out. Most importantly, this polymerization chemistry is applicable to existing bio-derived monomers as well as naturally-occurring compounds and polymers that can be readily modified to render them polymerizable by a cationic mechanism.

Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York, 12180, USA

E-mail: crivej@rpi.edu

Depicted in Scheme 1 is an abbreviated mechanism for the photopolymerization of a vinyl or heterocyclic monomer, M[5]. Among the most useful cationic photoinitiators are diaryliodonium and triarylsulfonium salts. The use of a diaryliodonium salt photoinitiator is exemplified in Scheme 1. Only a catalytic amount of the photoinitiator is required to carry out these photopolymerizations.

Irradiation of the photoinitiator with light (eq. 1) produces an excited species that decays to generate radicals, cations and cation-radicals. Interaction of the latter two species with the monomer or trace impurities gives the protonic acid, $HMtX_n$. When the anion, MtX_n^-, of the starting photoinitiator is selected from such non-nucleophilic species as PF_6^-, AsF_6^-, SbF_6^-, etc., the corresponding photogenerated acid is a "superacid" that is capable of rapidly and efficiently initiating the polymerization (eq. 2) of both vinyl and heterocyclic monomers. The cationic ring-opening photopolymerizations of epoxide-functional monomers is of particular interest and these monomers have found many commercial uses, for example, in coatings, adhesives and printing inks. We have been exploring the extension of this chemistry to biorenewable monomers. Specifically, double bonds are present in many different naturally occurring compounds and polymers that can be readily epoxidized to yield useful monomers and oligomers. For example, the epoxidation of terpenes obtained from the paper and pulp industries yields such monomers as α-pinene oxide, limonene mono- and dioxide that undergo facile photoinitiated cationic polymerization. Previously, we have also reported that epoxidized vegetable oils constitute a highly valuable potential source of novel monomers[6].

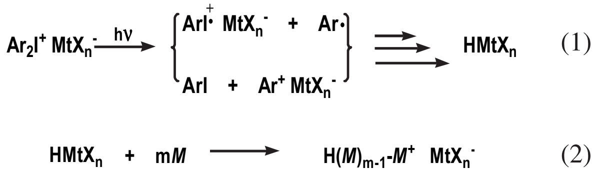
Since diaryliodonium and triarylsulfonium salts typically absorb in the region from 220–300 nm, irradiation with visible light is not effective for photopolymerization. Were it possible to use direct solar irradiation, there are many common activities such as home and boat building in which cationic photopolymerization could be employed together with biorenewable monomers. Sensitivity for various onium salt cationic photoinitiators has been achieved in the visible spectral region through the use of polynuclear aromatic hydrocarbon electron-transfer photosensitizers such as pyrene and perylene.[7] Scheme 2 portrays the mechanism by which electron-transfer photosensitization takes place using pyrene (PY).

Although polynuclear aromatic hydrocarbons are efficient photosensitizers, they are expensive, have a very limited spectral range, display poor solubility and are toxic. In recent years, Bi and Neckers[8] and Yagci and Hepuzer[9] have also reported the development of visible absorbing dye sensitizers for diaryliodonium salts. This article reports on the development of a novel, naturally occurring dye photosensitizer that addresses these shortcomings of present dye photosensitizer systems.

Results and Discussion

Electron-Transfer Photosenstization of Onium Salts

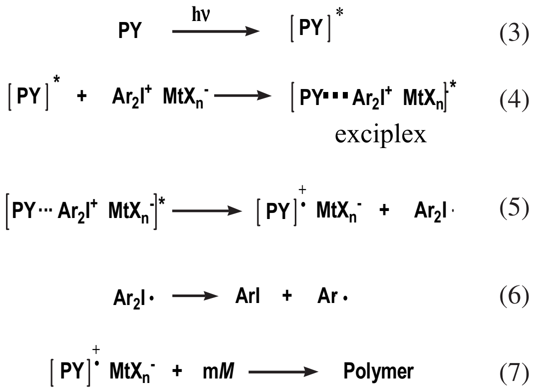
Several means for broadening the spectral sensitivity of onium salts are known [4],



$$\mathrm{Ar_2I^+\,MtX_n^-} \xrightarrow{h\nu} \left\{\begin{array}{l} \mathrm{Ar\overset{+}{I}\cdot\ MtX_n^- \;+\; Ar\cdot} \\ \mathrm{ArI \;+\; Ar^+\,MtX_n^-} \end{array}\right\} \rightrightarrows \mathrm{HMtX_n} \qquad (1)$$

$$\mathrm{HMtX_n} + \mathrm{m}M \longrightarrow \mathrm{H}(M)_{\mathrm{m-1}}\text{-}M^+\ \mathrm{MtX_n^-} \qquad (2)$$

Scheme 1.



Scheme 2.

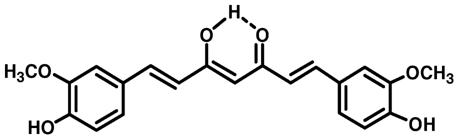
however, the most efficient method involves electron-transfer photosensitization as depicted in Scheme 2. Examination of this scheme leads to the realization that the overall process involves a photoinduced redox reaction in which an electron is transferred from the excited electron-donor to the onium salt resulting in the oxidation of the photosensitizer and a corresponding reduction of the onium salt. This may or may not involve the formation of an intermediate excited state complex between the photosensitizer and the onium salt. Photosensitizers must, therefore, be electron-rich molecules with strong absorption characteristics in the UV-visible spectral region that become good electron-donors in their excited states. An additional requirement in this instance is that a prospective photosensitizer must possess no groups that can interfere with the subsequent cationic polymerization. These criteria are met by polynuclear aromatic hydrocarbons, however unfortunately, the aforementioned drawbacks of these compounds preclude their use in all but academic studies. Accordingly, we have undertaken a search for additional novel classes of electron-transfer photosensitizers. To pursue this work, we required a method for rapidly screening potential photosensitizers.

Rehm and Weller[10,11] recognized the redox nature of the electron-transfer photosensitization and expressed this well-known relationship in equation 8 shown below.

$$\Delta G = \left(E^{ox}_{sens} - E^{red}_{onium}\right) - E^{*} \qquad (8)$$

This equation relates the free energy that drives the photosensitization process to the respective oxidation potential of the ground (E^{ox}_{sens}) and excited photosensitizer (E^{*}) and the reduction potential of the onium salt (E^{red}_{onium}). If these latter values are known, it is possible to calculate with good probability whether or not electron-transfer photosensitization is favorable for a given prospective photosensitizer-onium salt pair. While the reduction potentials of onium salts have been determined, the corresponding oxidation potentials of many prospective photosensitizers have not been measured. In this laboratory, we have employed a new analytical method, optical pyrometry (OP), that allows the very rapid screening of prospective photosensitizer compounds[12]. This technique is based on the principle that if a monomer containing an onium salt and a prospective photosensitizer is irradiated with long wavelength light, photosensitization will result in rapid, exothermic polymerization. The polymerization can be detected using the optical pyrometer by the resulting temperature rise in the sample. Details of the construction of the OP apparatus and sampling procedures were published previously.[13] In this work, optical pyrometry was also used to follow the course of the photosensitized polymerization reactions in real-time.

Turmeric is a well-known spice and coloring agent widely employed in India and throughout Southeast Asia. Turmeric is obtained by grinding the rhizomes of the plant *Curcuma longa*. Extraction of raw turmeric with chloroform results in isolation of the intensely yellow dye, curcumin, whose structure is depicted below[14]. We have observed that curcumin can be further purified by recrystallization from isopropyl alcohol.



Curcumin

The ^{1}H-NMR spectrum of curcumin indicates that this compound exists almost completely in the hydrogen bond-stabilized enol form shown above that allows the extension of the conjugation throughout the molecule and provides, as depicted in Figure 1, strong absorption from 330–500 nm ($\lambda_{max} = 427$ nm; $\varepsilon = 55000$). Turmeric has been used as a foodstuff for literally thousands of years and its use in traditional medicine is well entrenched[15]. Curcumin displays excellent solubility in a variety of solvents and, most importantly, in a wide range of polar and non-polar monomers. We have found curcumin to be an efficient photosensitizer for the photolysis of diaryliodonium salts in the long wavelength UV-visible region of the spectrum.[16]

Figure 2 shows a Stern-Volmer plot of the quenching of the curcumin fluorescence by the diaryliodonium salt (4-n-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10 SbF_6). The linear relationship between the fluorescence intensity and the onium salt concentration is strong evidence for the electron-transfer mechanism depicted in Scheme 2. It is also worth noting that there is a strong visible color shift from yellow to orange in solutions containing both an onium salt and curcumin during photolysis that is indicative of the formation of the curcumin cation-radical and the further reaction of this species with

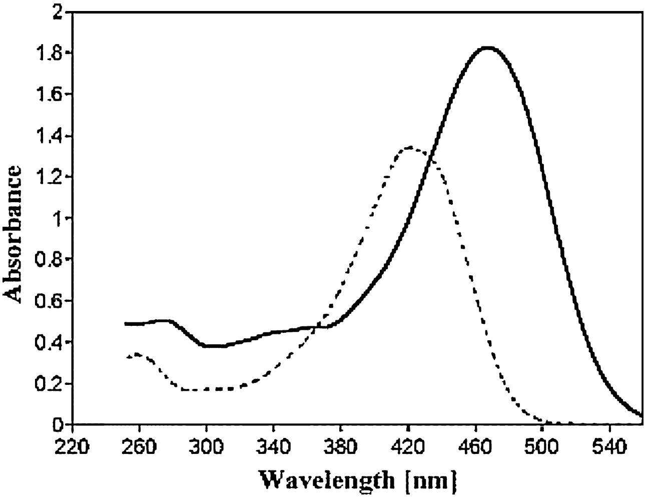


Figure 1.
Solid line obtained from 3.09 × 10 − 5 M curcumin in basic aqueous solution (NaOH 0.5 M). Dashed line obtained from 3.04 × 10 − 5 M curcumin in glacial acetic acid.[17,18]

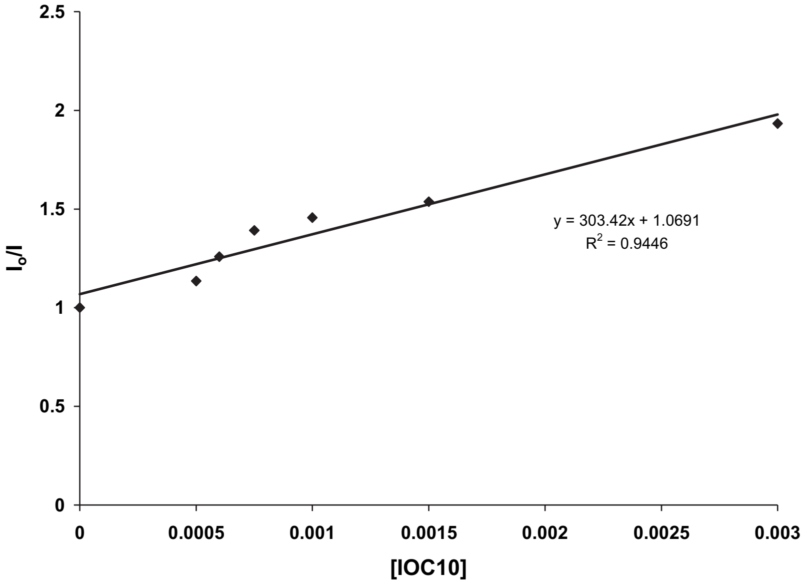
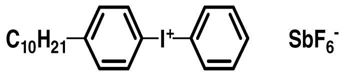


Figure 2.
Stern-Volmer plot of the quenching of curcumin (1×10^{-3} M) by (4-decyl-oxyphenyl)phenyliodonium hexafluoroantimonate (IOC10 SbF_6) in THF. (excitation wavelength 304 nm).

the solvent or monomer to form various secondary products.



IOC10 SbF_6

Cationic Photopolymerizations Using Curcumin Photosensitization

Curcumin is a naturally occurring dye photosensitizer for onium salts. Studies of the photosensitized cationic polymerizations of both synthetic and biorenewable monomers were conducted. The effect of the presence of curcumin on the photopolymerization of epoxidized terpene monomer, limonene-1,2-epoxide (limonene monoxide) is shown in Figure 3. The (OP) study was carried out using 1.0 mol% IOC-10 SbF_6 and employing relatively narrow-band, long wavelength UV irradiation (355–460 nm; midpoint 407 nm) that was generated using an optical filter. In the absence of curcumin, photopolymerization was not observed even after 500 s of irradiation. In contrast, when curcumin is present, immediate polymerization ensues indicating a strong photosensitization effect. Photosensitization by curcumin is quite efficient and a molar ratio of 1:10 with respect to curcumin and the onium salt photoinitiator appears to be nearly optimal.

Triarylsulfonium and dialkylphenacylsulfonium salts are easily prepared and their photosensitization by polynuclear aromatic hydrocarbons has been demonstrated[19–21]. While we observed that curcumin is a photosensitizer for these two classes of cationic photoinitiators, its efficiency is considerably less than observed for diaryliodonium salts. Presumably, this is because the reduction potentials for sulfonium salt photoinitiators are higher than for diaryliodonium salts[22].

The effects of curcumin on the photopolymerizations of several other cationically polymerizable monomers were also briefly examined. An OP study of the curcumin photosensitized polymerization of the terpene

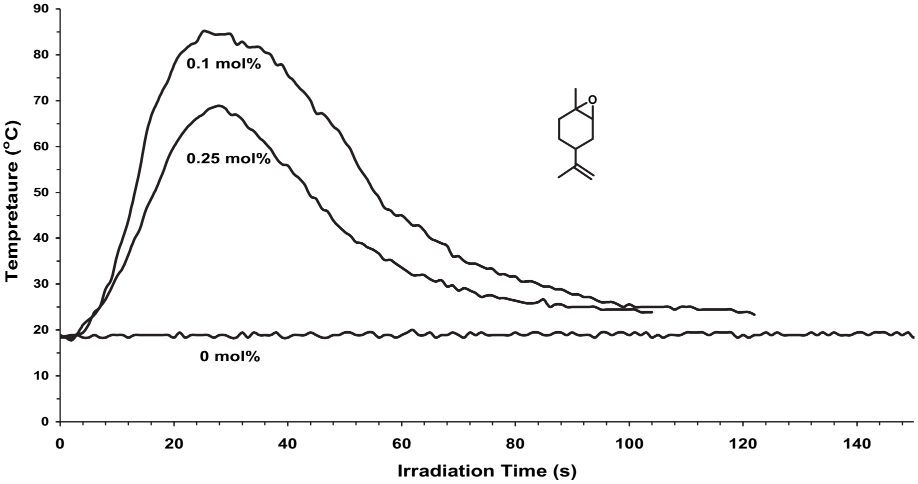


Figure 3.
OP study of the photopolymerization of limonene-1,2-epoxide with 1.0 mol% IOC10 SbF_6 in the absence of a photosensitizer and in the presence of 0.1 mol% and 0.25 mol% curcumin mol% photosensitizer. (light intensity 395 mJ/cm^2 min, 407 nm filter).

diepoxide, limonene dioxide, is shown in Figure 4. For comparison, Figure 3 also contains a study conducted in the absence of curcumin. Results similar to those obtained for limonene-1,2-epoxide were observed.

Oxetanes have similar ring strain energies as epoxides and, for that reason, display similar reactivities in photoinitiated cationic ring-opening polymerizations. An OP study of the polymerization of 3-ethyl-3-phenoxymethyloxetane (POX) is displayed in Figure 5. In the presence of curcumin, POX displays a long induction period followed by very rapid, highly exothermic polymerization. The same effect has been noted by Sasaki[23] for unsensitized photopolymerizations of this monomer carried out using short wavelength UV light. In a recent paper[24], we have shown that oxetane monomers such as POX which display long induction periods undergo frontal polymerizations. A mechanism was proposed to explain this behavior. Figure 5 shows that in the absence of curcumin, POX does not polymerize under the same irradiation conditions of this experiment.

Another highly interesting series of biorenewable monomers is epoxidized vegetable oils. A wide variety of unsaturated vegetable oils are available from common crop sources[25]. The structures of these oils vary greatly with respect to the number and placement of the double bonds and other functional groups such as hydroxyl groups may also be present. These oils can be readily epoxidized using environmentally benign methods such as with hydrogen peroxide in the presence of a tungsten complex as a catalyst[6,26] or by enzymatic epoxidation[27]. An example of such a material is epoxidized linseed oil. This monomer typically has 6-7 polymerizable epoxy groups per molecule and consequently a highly crosslinked network is obtained on polymerization. A comparison using OP between the photopolymerization of epoxidized linseed oil carried out in the presence and absence of curcumin is given in Figure 6. As the study shows, epoxidized linseed oil displays excellent reactivity under photosensitization by curcumin.

In recent years, several species of plants have been discovered that produce epoxidized triglycierides in high yields[28,29]. We have demonstrated that two of these oils isolated from the plants, *Vernonia galamensis* and *Euphorbia lagascae*, are quite

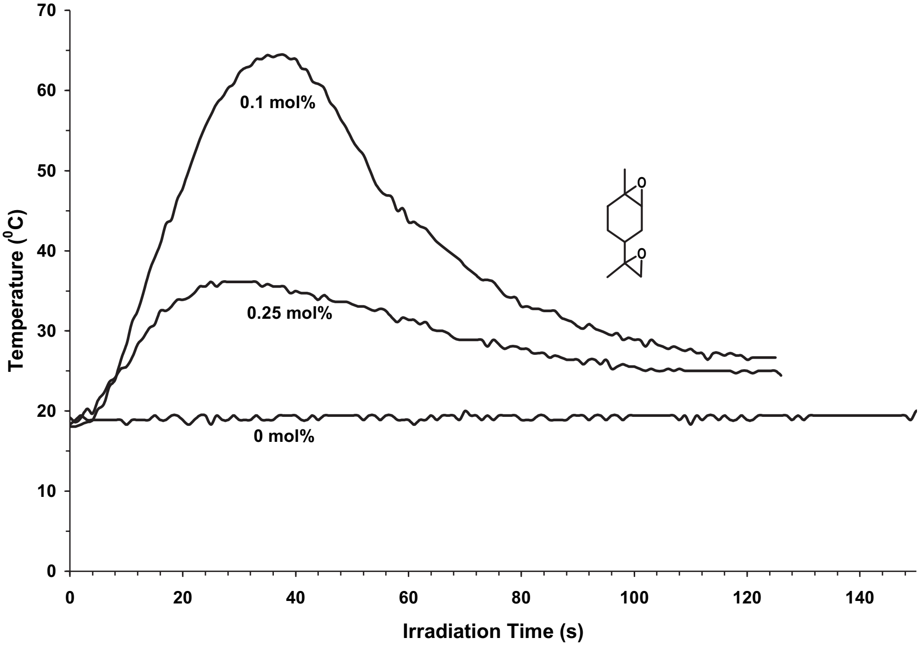


Figure 4.
OP study of the photopolymerization of limonene-dioxide with 1.0 mol% IOC10 SbF_6 in the absence of a photosensitizer and in the presence of 0.1 mol% and 0.25 mol% curcumin mol% photosensitizer. (light intensity 395 mJ/cm^2 min, 407 nm filter).

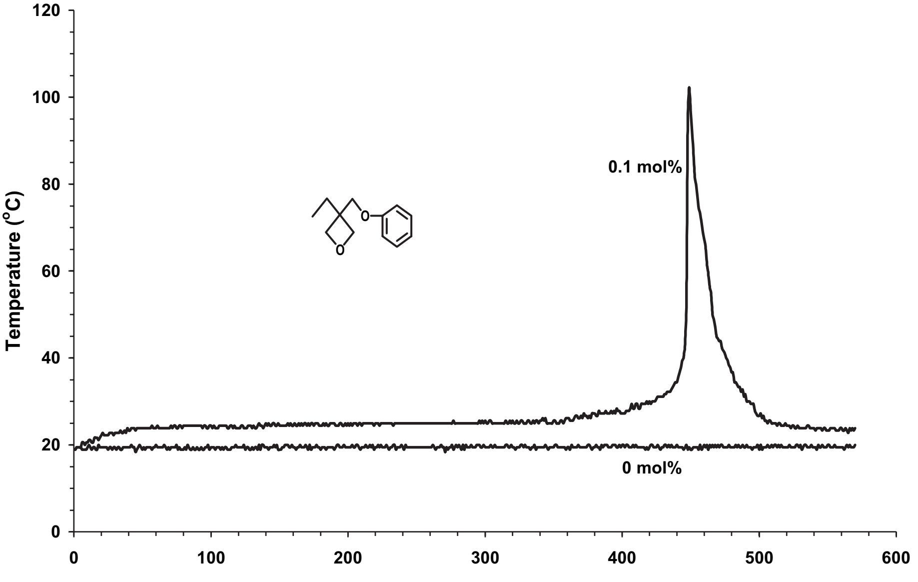
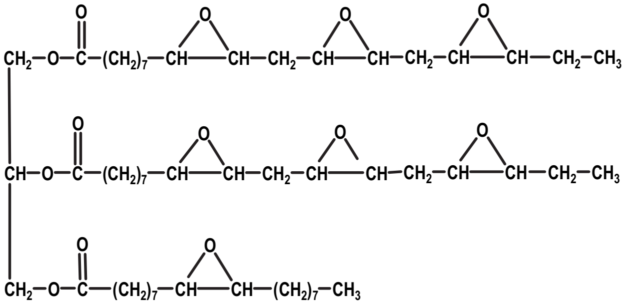


Figure 5.
Photopolymerization of POX with 1.0 mol% IOC10 SbF_6 in the absence of a photosensitizer and in the presence of 0.1 mol% curcumin mol% photosensitizer. (light intensity 850 mJ/cm^2 min, 407 nm filter).



Epoxidized linseed oil

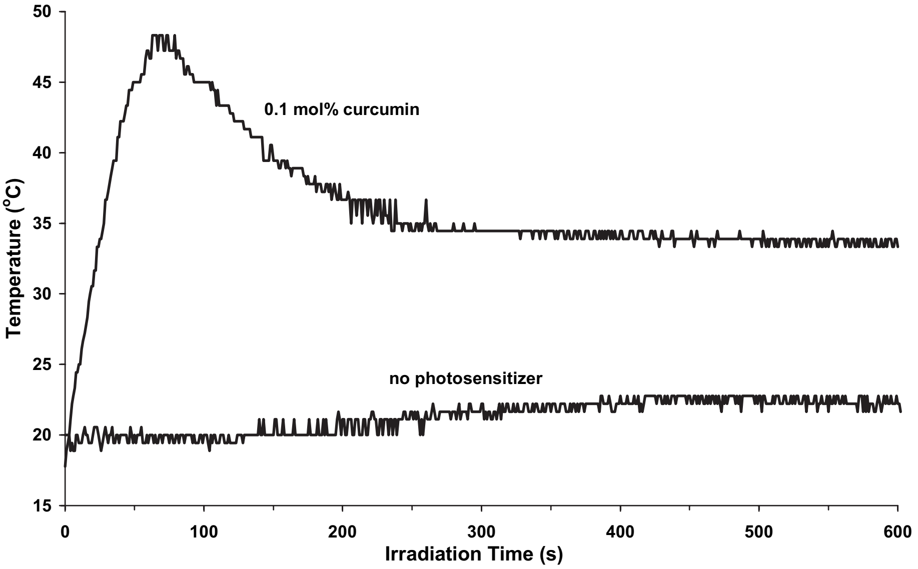


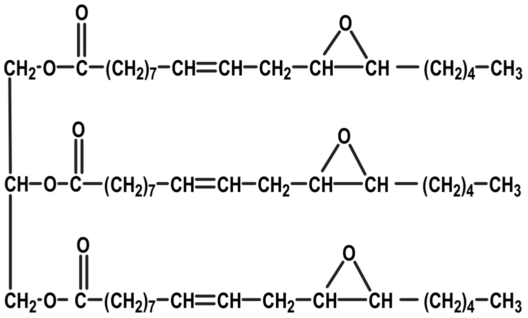
Figure 6.
OP study of the photopolymerization of epoxidized linseed oil in the presence and absence of curcumin (1.0 mol% IOC-10 SbF_6, light intensity 1500 mJ/cm^2 min, 407 nm filter).

reactive and can be directly used in cationic photopolymerizations[30]. Figure 7 shows the pronounced photosensitizing effect of curcumin on the photopolymerization of *Vernonia galamensis* oil with IOC-10 SbF_6 as the photoinitiator. Although this triglycieride contains only three epoxy groups per molecule, its reactivity is nearly as high as epoxidized linseed oil.

A report by Swedish workers[31] that the genes responsible for epoxidation in the above plants have been cloned and successfully expressed in other plants is very exciting. This opens the very real prospects that other, common and highly productive crops could also be induced to produce epoxidized oils. The possibilities for plantations of crops designed expressly for the production of monomers for use in plastics appears brighter and closer.

Curcumin Photosensitized Solar Polymerizations

The application of curcumin as a dye photosensitizer using UV irradiation for



Vernonia galamensis oil

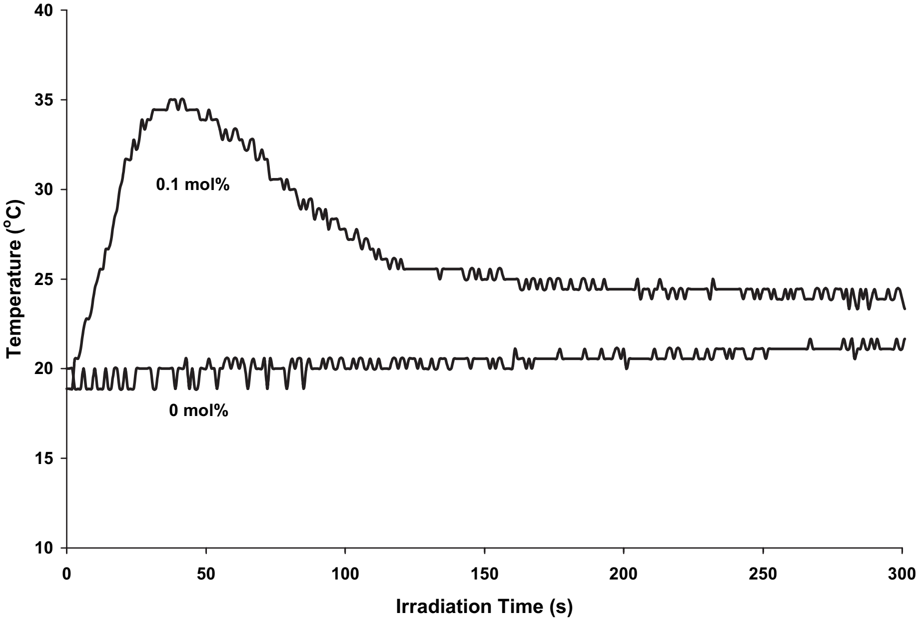


Figure 7.
Photopolymerization of Vernonia galamensis linseed oil carried out in the presence and absence of curcumin (1.0 mol% IOC-10 SbF_6, light intensity 800 mJ/cm^2 min, 407 nm filter).

the photopolymerization of synthetic and biorenewable monomers has been described. However, as pointed out, curcumin also absorbs strongly at visible wavelengths and it seemed worthwhile to attempt photosensitized cationic polymerizations using solar irradiation. Further, we wished to demonstrate several practical aspects of the use of this chemistry. Accordingly, epoxidized linseed oil containing 1.0 mol% IOC-10 SbF_6 and 0.1 mol% curcumin was used to impregnate glass cloth and then arranged in flat layers to make a laminate or wound around a mandrel to form a tube. The four-ply laminates were exposed to direct solar irradiation for 10 minutes at Troy, New York (latitude 42° North) on April 6, 2005 at 13:00–15:00 h. The ambient temperature during the solar exposure was 25 °C. After 5 minutes of continuous solar irradiation, the composites were dry to the touch. Irradiation was continued for an additional 5 minutes

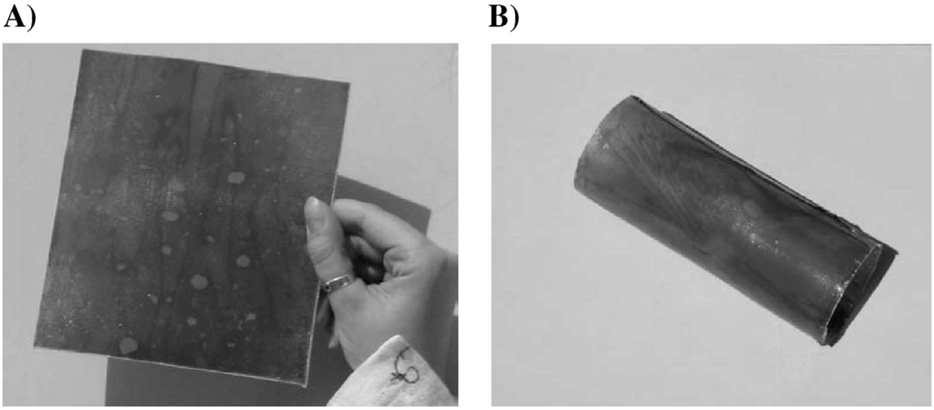


Figure 8.
8A and 8B. Composite glass laminate and tube produced by solar irradiation of epoxidized linseed oil using curcumin as a photosensitizer.

to ensure completion of the polymerization. Figure 8A and 8B show the two fully hardened composites that were produced.

There are many applications of this technology. For example, using solar irradiation, one can use the biorenewable monomers described earlier in this article to fabricate composite boats, building and roofing panels, as well as conduits for water and sewage. Medical applications include adhesives for catheters and casts and splints. Dental composite fillings would take advantage of the fact that both monomers and photosensitizer are nontoxic and visible light is not damaging to tissues. Most attractive of all is the possibility that all the materials required with the exception of the photoinitiator could be obtained from locally grown plants.

Conclusions

Curcumin, a naturally occurring dye obtained from the common spice, turmeric, is a potent electron-transfer photosensitizer for the photolysis of onium salt cationic photoinitiators. Owing to its broad UV and visible absorption characteristics, lack of toxicity, excellent solubility and low cost, curcumin may find widespread use in cationic ring-opening and vinyl photopolymerizations. Especially attractive is the use of this dye photosensitizer for the solar induced polymerization of biorenewable monomers. Several examples of curcumin photosensitized polymerization of epoxidized terpenes and epoxidized vegetable oils were presented.

[1] P.T. Anastas, L.G. Heine, T.C. Williamson, *Green Chemical Syntheses and Processes*, ACS Symp. Ser. 767, **2000**, American Chemical Society, Washington, DC.
[2] P.T. Anastas, T.C. Williamson, *Green Chemistry: Designing Chemistry for the Environment*, ACS Symp. Ser. 626, **1996**, American Chemical Society, Washington, DC.
[3] P.T. Anastas, P.H. Bickart, M.M. Krichhoff, *Designing Safer Polymers*, **2000**, Wiley-Interscience, New York.
[4] J.V. Crivello, In: "*Ring Opening Polymerization*", D.J. Brunelle, editor, **1993**, Hanser Pub, Munich, p.157.
[5] M. Jang, J.V. Crivello, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3056.
[6] J.V. Crivello, R. Narayan, *Chem. Mater.* **1992**, 4(3), 692.
[7] J.V. Crivello, F. Jiang, *Chem. Mater.* **2002**, *14*, 4858.
[8] Y. Bi, D.C. Neckers, *Macromolecules* **1994**, *27*, 3683.
[9] Y. Yagci, Y. Hepuzer, *Macromolecules* **1999**, *32*, 6367.
[10] D. Rehm, A. Weller, *Z. Phys. Chem. NF* **1970**, *69*, 183.
[11] S.P. Pappas, L.R. Gatechair, J.H. Jilek, *J. Polym. Sci., Part A: Polym. Chem.* **1979**, *11*, 1059.
[12] B. Falk, S. M Vallinas, J.V. Crivello*J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*(4), 579.
[13] J.V. Crivello, B. Falk, M.R. Zonca, Jr. *J. Appl. Polym. Sci.* **2004**, *92*(5), 3303.

[14] A. Anderson, M.S. Mitchell, R.S. Mohan, *J. Chem. Ed.* **2000**, *77*, 359.

[15] *The Merck Index, 13th Ed.*, M.J. O'Niel, A. Smith, P.E. Heckelman, editors, Whitehouse Station, NJ, **2001**, p. 2707.

[16] J.V. Crivello, U. Bulut, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5317.

[17] B. Mishra, K.I. Priyadarsini, M.K. Bhide, R.M. Kadam, H. Mohan, *Free Radical Res.* **2004**, *38*(4), 355.

[18] F. Zsila, Z. Bikadi, M. Simonyi, *Tetrahedron, Assym.* **2003**, *14*, 2433.

[19] J.V. Crivello and J.H.W. Lam, *J. Polym. Sci. Part A, Polym. Chem.* **1979**, *17*(4), 1059.

[20] J.V. Crivello, S. Kong*Macromolecules* **2000**, *33*(3), 825.

[21] J.V. Crivello, J.L. Lee, *Macromolecules* **1981**, *14*(5), 1141.

[22] Crivello, J.V. In: *UV Curing Science and Technology;*S.P. Pappas, Editor, Technology Marketing Corp.: Stamford, CN, 1978, p. 24.

[23] H. Sasaki, *Proc RadTech 2000 Technical Conference*, Baltimore, MD, April 9-12, **2000**, p. 61.

[24] B. Falk, M. R. Zonca, Jr. J.V. Crivello, *Macromol. Symp.* **2005**, *226*, 97–108.

[25] G.S. Jamieson, *Vegetable Fats and Oils, 2nd Ed.* **1943**, Reinhold Pub., New York.

[26] C. Venturello, R. D'Aloisio, *J. Org. Chem.* **1988**, *53*, 1553.

[27] M. Rusch gen. Klaas, S. Warwell, *J. Am. Oil Chem. Soc.* **1996**, *73*, 1453.

[28] L.H. Princen, *J. Coatings Techn.* **1977**, *49*(635), 88.

[29] F.R. Earle, *J. Am. Oil Chem. Soc.* **1970**, *47*, 510.

[30] J.V. Crivello, K.D. Carlson Macromol. Repts. **1996**, *A33* (Suppls. 5&6),251.

[31] M. Lee, M. Lenman, A. Banaś, M. Bafor, S. Singh, M. Schweizer, R. Nilsson, C. Liljenberg, A. Dahlqvist, P.-O. Gummeson, S. Sjödahl, A. Green, S. Stymne, *Science*, **1998**, *280*, 915.