

DOE/ER/12117--2

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Annual Performance Report

**CATIONICALLY POLYMERIZABLE MONOMERS
DERIVED FROM RENEWABLE SOURCES****DE-FG02-91ER12117**

October 1, 1992

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Objectives

The objectives of this project are to design and synthesize novel monomers which originate from renewable biological sources and to carry out their rapid, efficient, pollution-free and energy efficient cationic polymerization to useful products under the influence of ultraviolet light or heat. A further objective is to evaluate the biodegradation of the polymers which are produced.

A summary of the results of the past year's research on cationically polymerizable monomers derived from renewable sources are presented. Three major areas of investigation corresponding to the different classes of naturally occurring starting materials were investigated; epoxidized oils, epoxidized terpenes and natural rubber and vinyl ethers from alcohols and carbohydrates.

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Assessment of Performance

Most of the objectives outlined at the beginning of this project have been achieved in the case of the photopolymerizable epoxidized natural oils. These materials are available in large quantities at very low cost from a variety of commercial sources. These materials are also produced domestically and finding new uses can potentially provide more jobs and higher value added applications for these commodity agricultural products. We have further shown that improvements in the economics and the environmental impact of the epoxidation of these oils can be made. In addition, the use of photocurable epoxidized natural oils as coatings has been demonstrated in this laboratory. Further, we are currently working with industrial firms to implement this technology into several commercial applications. Although preliminary biodegradation studies have already been done, a cooperative program with the University of Connecticut has been initiated which is directed towards getting more quantitative results on the biodegradability of photopolymerized epoxidized natural oils.

Additional classes of monomers derived from carbohydrates and from terpenes and natural rubber are also being investigated. Recent work has shown that novel multifunctional propenyl ethers can be prepared by a simple, direct method. Further, the exceptionally high reactivity of these monomers makes them very attractive for high speed applications such as printing inks. Detailed studies have been conducted of the photopolymerization of these materials and novel mechanisms have been proposed to explain the outstanding reactivity of these new monomers.

Natural rubber and terpenes are yet another class of naturally occurring starting materials which are being used to prepare monomers and oligomers for photopolymerization. Successful application of the epoxidation methods developed for the natural oils has been applied to these materials. The photopolymerization of these monomers and oligomers is currently being studied.

Lastly, our first paper describing results on this DOE sponsored project has appeared in a respected scientific journal. Three other papers have been submitted and will appear in the future. One patent application has also been submitted for filing by Rensselaer Polytechnic Institute.

Results

In the following sections, a detailed description of the results in the three major areas of natural products-derived monomers is presented.

Epoxidized Oils

Previously, we reported that a wide variety of epoxidized natural oils can be photopolymerized using ultraviolet and visible light. We have further describe the use of these photopolymerizable oils to make coatings on wood, glass and metals. UV curing provides a rapid, low energy, environmentally safe method for the polymerization of these materials. Key to this technology has been the development of soluble, efficient cationic photoinitiators. During this research period, we have expanded our research into the following areas.

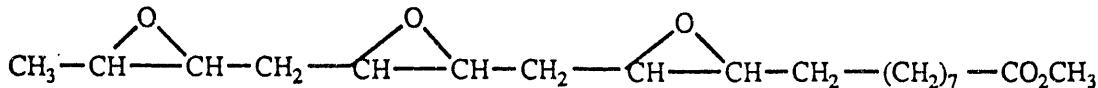
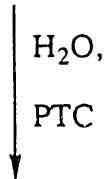
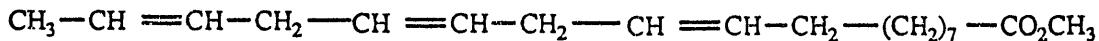
A. Further Studies of the Phase Transfer Epoxidation of Oils

We have found that the phase transfer method of epoxidation of natural unsaturated oils is a very facile and convenient method of preparing the corresponding epoxidized oils. Besides our interest in the photopolymerization of these oils, there is considerable commercial use of these material as plasticizers and as stabilizers for poly(vinyl chloride). Studies performed during the past six months have resulted in optimization of the phase transfer method which now allows the reaction to be stopped at any epoxidation level

desired. Considerable interest in the investigation of this method by ATO Chem Corporation has been expressed. ATO Chem currently markets both epoxidized soybean and epoxidized linseed oils and has been interested in our method because of its good economics and its excellent environmental compliance. The only byproduct is water. As a result, ATO Chem is evaluating samples of epoxidized soybean oil which we have sent them and comparing it with their present commercial product.

B. Other Epoxidized Derivatives of Natural Oils

Using transesterification reactions, it has been possible to prepare several novel derivatives of unsaturated fatty acids and to carry out their epoxidation. For example, transesterification of linseed oil with methanol gives rise to a mixture of methyl esters of linoleic and linolenic acids. These esters can then be epoxidized using phase transfer epoxidation. An example is shown in the following equation.



There is considerable potential for simple esters such as methyl linolenate. First, the functionality is high: since it contains three epoxy groups. Secondly, the ester has a low viscosity (~80 cps) as compared to 300-500 for the epoxidized triglyceride monomers. This means that this ester could be used as a reactive diluent to provide low viscosity materials for coating applications. UV curable epoxy materials which can be spray coated would be of considerable interest in the wood coatings industry.

C. Visible Light Cured Resins

We have now been conducting studies directed towards the photosensitization of the polymerization of epoxidized natural oils. Photosensitization makes it possible to use even sunlight for carrying out the conversion of these oils to plastic coatings, adhesives and encapsulants. Typically, the usual photoinitiator which is sensitive to UV light is employed together with a photosensitizer which absorbs in the visible region of the spectrum. The combination cures rapidly when irradiated using lamps which emit only in the visible region of the spectrum. Only very small amounts of the photosensitizer (0.1 weight %) are necessary. We have used perylene, pyrene and anthracene as photosensitizers in our studies. Photosensitization makes this technology accessible to even third world countries which can use sunlight to trigger the photopolymerization. The successful photosensitization of these resins also explains the use of photocurable epoxidized natural oils to many other potential application areas. One of these areas is described in the following section.

D. Use of Photocurable Epoxidized Natural Oils in Composite Applications

The ability to carry out visible light curing of epoxidized natural oils has allowed their use in composite applications. The main reason is the greater penetration depth of visible light as compared to UV light in organic resins. As a demonstration of this technology, this investigator, together with two students built a composite boat (a kyack) during the past summer using sunlight to accomplish the cure. A resin mixture consisting of 70% of epoxidized linseed oil and 30% of a synthetic commercially available epoxy resin (3,4-epoxycyclohexylmethyl 3'4'-epoxycyclohexane carboxylate) were combined with a sulfonium salt photoinitiator. The resin formulation was impregnated into glass cloth laid into a female mold. The impregnation was performed in a shop under illumination by

incandescent lamps. After three layers of impregnated glass were applied, the mold was moved outside into the sunlight. After 10 minutes exposure, the laminate was tack-free to the touch. The entire piece was removed from the mold after 30 minutes exposure to give the completed molded part. In this manner, the upper and lower halves of the kyack were fabricated. The halves were then joined by applying a resin impregnated tape to the midline of the kyack and once again exposing the assembly to sunlight.

The length of the kyack was 13.5 ft and weighed 30-35 lbs. The kyack was fully seaworthy and was used by the students in a local lake. Included together with this report is a slide showing the completed kyack. Besides demonstrating the use of UV curing of epoxidized natural oils in composites, this exercise has provided a valuable learning experience for the students. It has enabled them to directly apply this chemistry to a fully functional boat. We believe that this technology has considerable potential for use in boat building as well as in many other similar composite structures in which light weight and high strength are required. Studies are now under way to determine the mechanical properties of the visible light cured composite structures and to optimize the formulations.

E. Commercial Applications of UV Curable Epoxidized Natural Oils

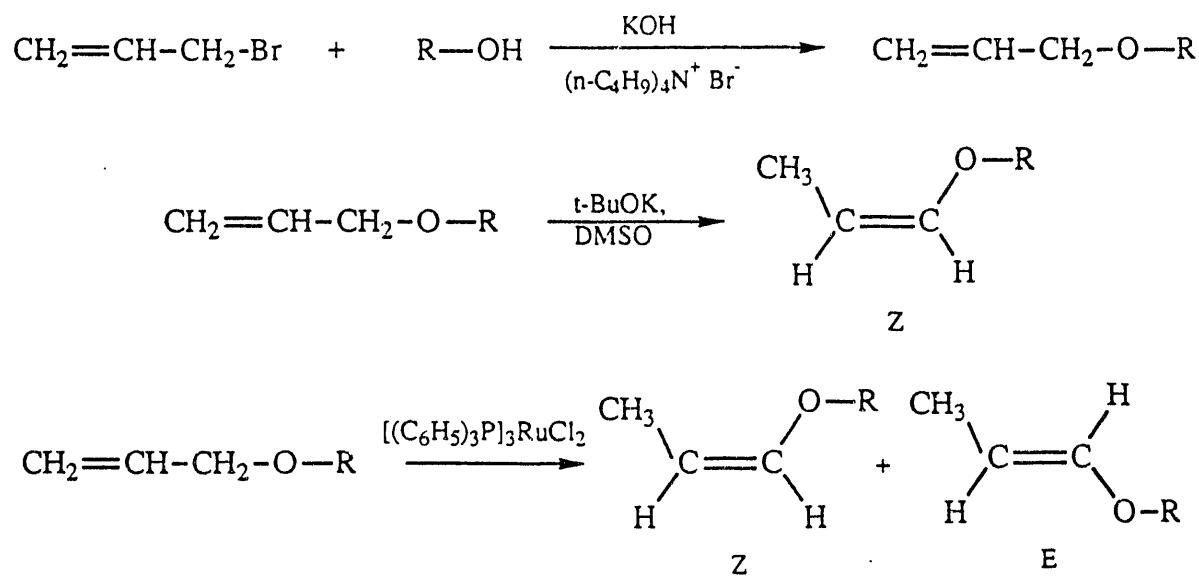
As part of this project, we have been endeavoring to transition this technology to interested companies involved in UV curing technology. The Alcoa Corporation has tested our photopolymerized oils on aluminum as beverage coatings. Preliminary results look promising. The inherent low cost and toxicity of the epoxidized natural oils is a big factor in the potential commercialization of this technology. We continue to work with Alcoa to further refine our formulations to provide the spectrum of mechanical and chemical characteristics which are required in this application.

F. Biodegradability

An integral portion of this project involves the determination of the environmental impact of polymers derived from naturally monomers. Workers at the University of Connecticut have had a long-standing program in biodegradable polymers. As a result, they have a cooperative program involving both chemists and biochemists and have worked out various protocols for the assay of biodegradation under various conditions. The University of Connecticut has agreed to conduct studies on samples of our photopolymerized epoxidized oils. This program will be initiated in the very near future.

New Reactive Monomers From Alcohols and Carbohydrates

A series of novel multifunctional alcohols such as sugars, glycerol and ethylene glycol which are derived from renewable sources have been converted to highly reactive monomers using unique chemistry developed in this laboratory. The general route for the synthesis of these monomers is given in the following series of equations.



The alcohols are subjected to treatment with allyl chloride or allyl bromide to make the corresponding allyl ethers and then catalytically rearranged to the corresponding multifunctional propenyl ethers. Two catalysts were used; KOH in DMSO and tristriphenylphosphineruthenium(II) dichloride. We have extensively studied this isomerization reaction and find that it proceeds to completion within 2-4 hours at 120°C. Thus, a wide variety of interesting cationically polymerizable monomers can be prepared using alcohols derived from natural sources. For example, glycerol from fats and carbohydrates can be employed to prepare the corresponding multifunctional propenyl ethers. Shown in Table 1 are a list of the propenyl ether monomers which were prepared using this chemistry.

The method shown above provides a new, very simple approach to the preparation of multifunctional propenyl ethers which would make them readily available for potential commercial use. Vinyl ether monomers with related structures are being commercially promoted as UV curable substrates. However, only two monomers are available and these are very costly. As noted, in Table 1, the range of propenyl ethers which can be prepared by our new method is very broad and should provide a spectrum of different properties. Furthermore, the method is inherently inexpensive and the yields are nearly quantitative.

The new propenyl ether monomers are highly reactive substrates when combined with our cationic photoinitiators. In comparison with the epoxidized natural oils they are more reactive by a factor of at least 100. A comprehensive, quantitative study of the reactivity of these monomers has been completed which shows that the reactivity is comparable with vinyl ethers in photoinitiated cationic polymerization. This makes them among the most reactive monomers yet discovered for use in UV curing. As part of our study, we discovered that in addition to the cationic polymerization, a free radical process is also occurring when these monomers are irradiated. The overall effect is that the rate of polymerization is

greatly enhanced in the presence of certain photoinitiators having low reduction potentials. This effect had never been observed previously and we are now making use of this "synergistic effect" to design both monomers and photoinitiators with enhanced reactivities. By analogy with the corresponding vinyl ethers, we would expect that the toxicology of these propenyl ethers would be similarly very low.

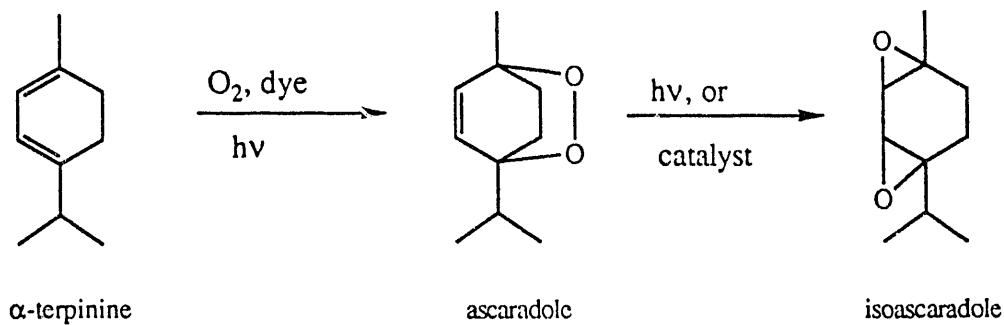
Because of the many attractive features of these new monomers, we believe that they have a very promising future as commercial products. Among the many applications of interest are paper coating applications such as photocurable inks and adhesives which require very high cure rates.

Epoxidized Natural Rubber and Terpenes

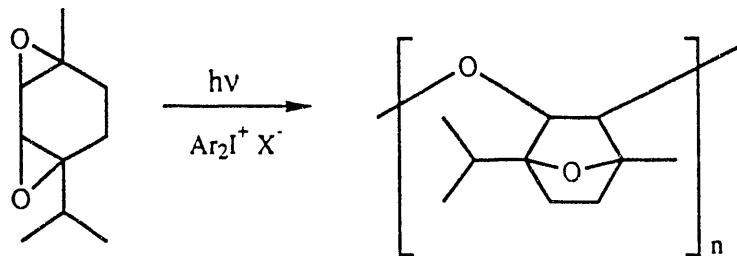
Natural rubber is available from many different plant sources. We are now able to conduct the facile, phase transfer catalyzed epoxidation of this material in a controlled manner to introduce as many or as few epoxy groups into the molecule as desired. We have observed that this material is rapidly crosslinked on UV irradiation and in the presence of a photoinitiator to beautiful transparent, elastomeric films. This represents a new photovulcanization process. Studies are now in progress to determine the best photoinitiators and UV irradiation conditions under which to carry out the polymerization of these resins. We are also preparing other epoxidized synthetic rubbers to compare them with the natural products. An interesting observation has been the discovery that epoxidized oils and epoxidized natural rubber are mutually soluble. We have also observed that they may be cophotopolymerized using soluble cationic photoinitiators. These "hybrid" natural systems may have interesting and unique properties which may be of use as coatings.

Interesting monomers can also be prepared by the epoxidation of terpenes. Work in this laboratory has been progressing directed

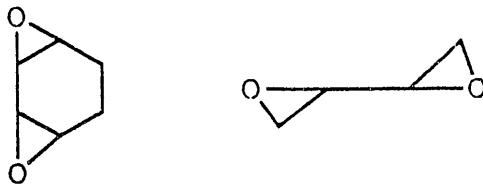
towards the development of novel, high reactivity monomers by simple techniques. In this regard, α -terpinene, derived from terpentine can be photooxidized to give the endo peroxide (ascaradole) which can readily be rearranged to give the diepoxide, isoascaridole. This transformation is shown in the following equation.



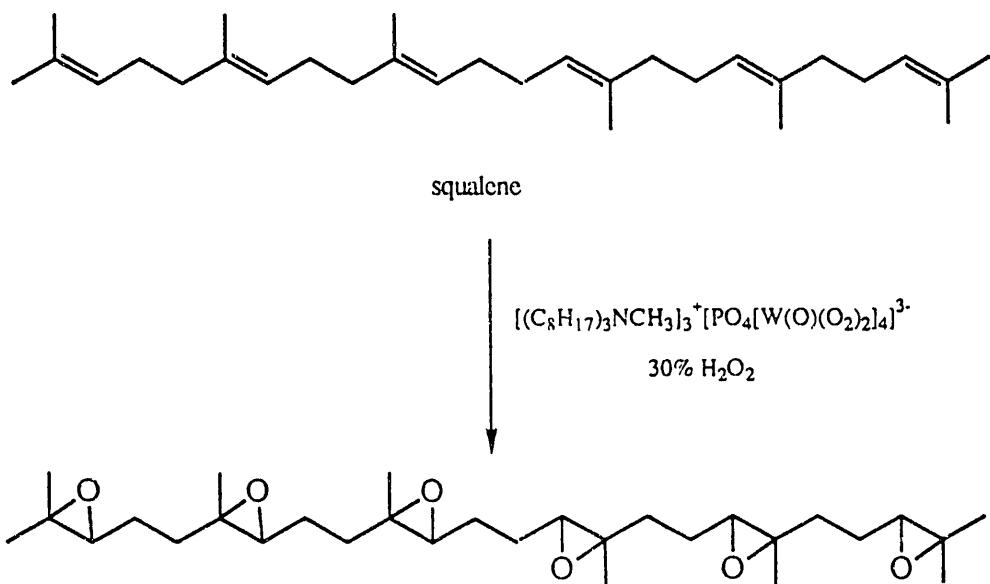
The photopolymerization of isoascaridole was studied in some detail. It was observed that the reaction took place very rapidly as detected by real time infrared analysis. However, the polymerization does not yield high molecular weight crosslinked polymers. Instead, we have been able to show that polymerization proceeds by simultaneous ring-opening of both epoxides to give a polymer containing tetrahydrofuran rings in the backbone. This reaction is shown below.



Interestingly, other 1,3-diepoxides, such as those listed below, polymerize by the normal independent ring-opening of each epoxide group.



Another naturally occurring polyterpene of interest is squalene. This molecule contains six double bonds which can smoothly be epoxidized using the phase transfer method.



This epoxide undergoes rapid cationic photopolymerization to give colorless, transparent crosslinked films. Squalene hexaepoxide serves as an interesting model compound for natural rubber since it has the same basic structure. A detailed study is in progress to optimize the various parameters of the cationic photopolymerization including; the photoinitiator type, concentration and the irradiation conditions for this monomer.

Publications and Patents

Part of this program involves the dissemination of the results of the research both to industries which can make use of the technology and also to other researchers in the field. In the above sections we

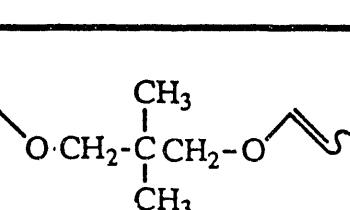
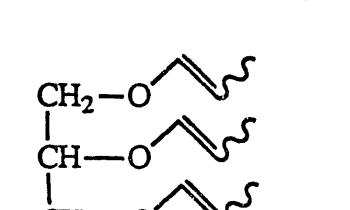
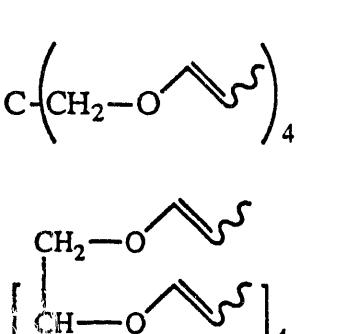
have detailed several cases in which we are transitioning particular portions of this work to various companies already engaged in either the synthesis of new materials or in the use of UV curing materials. In addition, we have been actively engaged in the publication of our work. This past April, a paper describing our work in the area of UV curable epoxidized natural oils was presented at the Radtech '92 Meeting held in Boston. This paper generated much interest both at the conference and in follow up correspondence. Subsequently, a full paper describing this research appeared in the Chemistry of Materials (an American Chemical Society journal). In addition, there was much popular press attention paid to this work. An interview and demonstration were broadcast on television by CNN. In addition, based on an interview with the Associated Press, articles appeared in more than 100 papers and magazines both domestic and international describing this DOE sponsored project. In each case, the DOE was prominently featured for their sponsorship of this project.

We continue to publish other portions of our results. Three papers describing the propenyl ether chemistry were recently submitted to the Journal of Polymer Chemistry. We are now awaiting response from the reviewers. In addition, a patent has been submitted for filing by the university describing these new propenyl ether monomers and the methods for their preparation.

**Structure and Properties of Multifunctional
Propenyl Ethers**

Structure	Elemental Analysis		
	%C	%H	%O
	Fnd: 69.30 Calc: 69.55	7.47 7.30	
	Fnd: 67.17 Calc: 67.57	9.94 9.92	
	Fnd: 70.66 Calc: 70.55	11.02 10.66	
	Fnd: 72.32 Calc: 72.68	11.28 11.11	16.73 16.16
	Fnd: 74.32 Calc: 74.34	11.39 11.50	14.95 14.16
	Fnd: 75.40 Calc: 75.54	12.03 11.89	
	Fnd: 64.27 Calc: 64.52	9.57 9.68	25.81 25.81
	Fnd: 62.68 Calc: 62.59	9.75 9.63	
	Fnd: 60.99 Calc: 61.29	9.81 9.55	

Structure and Properties of Multifunctional Propenyl Ethers

Structure	Elemental Analysis		
	%C	%H	%O
	Fnd: 71.25 Calc: 71.70	10.91 10.94	17.97 17.36
$C_2H_5-C\left(CH_2-O\right)_3$	Calc: 70.47 Fnd: 70.87	10.47 10.24	19.32 18.90
	Fnd: 67.88 Calc: 67.89	9.73 9.50	
$C\left(CH_2-O\right)_4$	Fnd: 69.11 Calc: 68.89	9.81 9.52	
	Fnd: 67.88 Calc: 68.22	9.11 9.06	

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