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FINAL REPORT

U.S. Department of Energy Grant

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Cationically Polymerizable Monomers Derived From Renewable Sources

Objectives

The objective of this proposal was to make use of a wide variety of products obtained from plant sources as monomers for the direct production of polymers which can be used for a wide range of plastic applications. In particular, high volume American agricultural products such as soybean, cotton or linseed oils or forestry products such as lignin and cellulose derived chemicals were targeted fro used either directly or with very slight modification for the production of the plastics. Further, we proposed to polymerize these monomers using rapid, efficient, pollution-free and energy efficient cationic photopolymerization techniques.

Rationale For This Proposal

The development of reactive monomers from renewable sources addresses a number of energy, economic, environmental and social issues currently of major importance to the United States of America and to the world. First, in our current materials based technological society, polymers occupy a prominent roll. From the fibers which go into the clothes we wear, to the plastics components which house our radios and TV's, to the bumpers and tires on our automobiles and the polymer additives in the food we eat, our lives are immeasurably enriched by the presence of polymers. Today, the basis of such synthetic materials is petroleum. U.S. production of

synthetic polymers in 1988 amounted to 69 billion pounds.[1] Replacement of even a small portion of this amount with polymers derived from biomass feedstocks would conserve dwindling and costly petroleum resources. At the same time, the balance of payments due to the large importation of oil could be partially offset by the utilization of domestic generated biomass feedstocks for plastics manufacture. Further, the process of the production of monomers from renewable sources would not only bolster local agriculture, forestry and related industries within this country, but also offer new business opportunities for the chemicals industry. This proposal details several approaches to the development of several feedstock materials as directly isolated from plant sources for use as monomers in polymer synthesis. Other schemes are described by which practical, simple, one and two step reactions can be carried out on the naturally derived materials to convert them into reactive and useful monomers.

A second impetus for the development of monomers and polymers from renewable sources derives from considerations for their disposal. Plastic items, especially film from packaging applications constitutes a considerable waste disposal problem in technically developed societies today. Since at present, conventional petroleum-based plastics are used which are essentially biologically nondegradable, they tend to accumulate in the environment. For example, packaging materials which amount to almost 2.8 billion pounds annually now constitute 30% of the volume of municipal waste.[2] Polymers derived from natural sources often contain functional groups which make them highly susceptible to biological degradation. If acceptable properties can be designed into such materials, they would find a much needed niche within the family of existing polymeric materials. All of the materials described in this proposal are potentially biodegradable and the biodegradability of those polymer materials which are generated during the course of this research will be determined.

Lastly and most importantly, one requires a means for conveniently polymerizing the renewable monomers or modified polymers. In this proposal is described in detail the development of novel photo and thermal initiators for cationic polymerization which has been recently carried out in these laboratories. It is this new technology, which for the first time makes it possible to polymerize cationically polymerizable monomers rapidly, homogeneously, with low energy requirements and without pollution. Applications of this chemistry using available totally synthetic epoxide and vinyl ether monomers is currently a commercial reality and is being practiced on a large industrial scale. The results of this U.S. DOE grant has generated means by which this technology may also be applied to a wide number of potential monomers which can be derived from renewable sources. As a result of these factors, the chemistry developed during the course of this grant is attracting considerable commercial interest.

Executive Summary of Results

The goals outlined above have been achieved. All of the results have been documented either in previous reports to DOE or have been published in first rate journals. The journal articles are attached to this report. This final report contains a point-by-point summary of the major technical and educational accomplishments which were acheived as a direct result of this grant.

The work under the sponsorship of U.S. DOE can be devided into four main parts which relate to the four different classes of naturally derived substrates which were employed for monomer synthesis, namely: lipids, terpenes, carbohydrates and lignin.

Lipid (Unsaturated Vegetable Oil) Derived Monomers

1. Eleven different unsaturated vegetable oils were obtained and epoxidized. These materials are readily obtainable and inexpensive substrates for use as biorenewable monomers. All of the oils used

were either directly products of American agriculture or under currently under study by the U.S. Dept. of Agriculture as potential large scale crop development.

2. A novel, phase transfer epoxidation of unsaturated vegetable oils was developed which has the following advantages: a) it is quantitative b) inexpensive c) results in no air or water pollution.

3. Epoxidized oils have been obtained directly from natural sources (vernonia galamensis) and were found to be active as monomers.

4. The photoinitiated cationic polymerization of the epoxidized lipids were studied. Optimal irradiation conditions, photoinitiator concentrations and epoxy contents were determined.

5. The use of the epoxidized oils as rapidly curing coatings was demonstrated.

6. Composite applications for photocurable epoxidized lipids were also explored. It was found that composites with load bearing mechanical properties could be obtained by simple layup techniques. Composites with ten layers of glass fibers could be produced by using solar irradiation only. The mechanical properties of composites with various blends of epoxidized oils and synthetic epoxide monomers were measured. Demonstration construction of a boat, building panels and a arm cast were carried out. All of these items were produced using solar irradiation.

Terpenes

Terpenes are derivatives of isoprene. These materials are very common in nature and occur in many forms. Two major sources of small molecule terpenes are terpentine, derived from wood and paper making and citrus peels. As a result, these materials are readily available and inexpensive.

1. Simple terpenes; α-terpinene, γ-terpinene and limonene were epoxidized to give their corresponding diepoxy derivatives. These compounds are low viscosity, colorless liquids which could potentially be used in many photocurable epoxy coating, adhesive and ink formulations.

2. The photoinitiated cationic polymerization of these monomers was thoroughly studied. It was observed that while γ-terpinene and limonene diepoxides undergo facile and efficient crosslinking photopolymerization to give transparent, crosslinked films, α-terpinene does not polymerize.

3. Limonene diepoxide and γ-terpinene diepoxide can be used in many practical applications and because of their low viscosity and high reactivity are being employed as reactive diluents.

4. Natural rubber (poly-cis-isoprene) which is a polyterpene is in excess supply. This polymer has been successfully epoxidized using the above described phase transfer catalyzed epoxidation methodology developed during work on this grant. This method allows the controlled introduction of as many epoxide groups as desired into the polymer backbone.

5. Squalene, a natually derived triterpene was also obtained and exhaustively epoxidized using phase transfer epoxidation to give the hexaepoxide.

6. The photoinitiated cationic polymerization of poly(cis-isoprene oxides) and squalene hexaepoxide were studied. All of these epoxides were observed to undergo rapid, efficient crosslinking photopolymerization.

7. Flexible, transparent films were obtained from the photopolymerized epoxidized natual rubber. These materials have many potential applications as rapidly curing coatings and adhesives.

Carbohydrates

Carbohydrates are the most abundant organic molecules on earth. We have developed novel chemistry which allows us to take simple molecules like glucose derived from carbohydrates and convert them to highly reactive monomers. These monomers can be employed for very rapid polymerizations and are especially useful as coatings and printing inks.

1. Novel and general chemistry was developed which allowed the direct isomerization of allyl ethers of carbohydrates to the corresponding 1-propenyl ethers.

2. The polymerization of these monomers were studied and it was observed that they are among the most reactive monomers yet prepared.

3. This chemistry was extended to the synthesis of 1-butenyl ethers derived from the isomerization of crotyl ethers. In this case, both portions of the monomers were derived from biological sources.

4. Further extention of the above general chemistry was made for the conversion of simple alcohols, and in particular, glycerol to produce glycerol tri-1-propenyl ether and glycerol tri-1-butenyl ether.

Lignin

Lignin is a waste product derived from pulp and paper manufacture. It is available in very large quantitites and is usually burned to recover the heat value. Lignin derived chemicals have received little attention because to date there has been no large market for these materials.

1. Eugenol is available in large quantities from lignin. We have carried out the isomerization of eugenol to isoeugenol using base and ruthenium complex catalysis.

2. Isoeugenol was employed for the synthesis of a wide variety of monomers by condensation with alkyl halides. The monomers were thoroughly characterized.

3. Photoolymerization of isoeugenol-derived monomers was carried out and it was observed that these monomers were highly reactive and gave tough, crosslinked films.

Educational and Commercial Implications of This Grant

During the course of this U.S. DOE sponsored grant, two students received their doctorates and three postdoctoral coworkers received postgraduate training. In addition, two undergraduate students received summer training. Nine published articles in first rate journals have appeared. Two additional articles are still in press. Reports of our work appeared in over 100 newspapers and scientific magazines and on a CNN television report.

As a result of the above publications and the press we have received, there has been a great deal of commercial interest in the use of biologically derived monomers in photoinitiated cationic polymerization. Several companies such as Elf-Atochem and Sartomer, Inc. are currently engaged in projects directed towards commericallization of the monomers. A number of other companies are currently employing epoxidized vegetable oils in UV curable coating formulations. One high volume use is in beverage can coatings. This has resulted in new business for both producers of these oils and for the producers of the coatings. Ultimately, American farmers will benefit from the increased value of their oil seed products.

As the present grant concludes, work in this area continues under the sponsorship of the U.S. Department of Agriculture and the Caschem Co. We anticipate that due to the commercial interest in this area, we will be active in the area of monomers derived from renewable sources for some years to come.

Acknowledgment

As the present grant expires, this principal investigator wishes to express his gratitude to Dr. Walter Polansky, Mr. Duane Barney and their staff and the U.S. Department of Energy for their support. I am especially appreciative of the faith which these persons placed in us at the outset of the project in spite of some critical comments by the reviewers. Should their be any follow up questions concerning this summary report, I will be happy to answer them.