

**Small Business Innovation Research (SBIR) Program
Proposal Cover Sheet**

Topic Number: 24c

Proposal Title: ENCAPSULANT FOR BROADBAND MULTIUNCTION SOLAR CELLS

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Proposed Cost: \$100,000

Phase: I

Duration: 9 months

Project Manager/Principal Investigator

Corporate Official (Business)

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Proprietary Information: N/A

Identification and Significance of the Problem or Opportunity, and Technical Approach

This proposal seeks a novel encapsulant with superior environmental stability using a polymeric system, which is designed to serve as a superstrate for both single and multi-junction solar cells. It recognizes that reliability and durability are fundamental to the economic success of any photovoltaic solar panel system. It envisions an encapsulant that can last 30 years on a rooftop in all climates, surviving UV exposure, temperature cycling, freezing and thawing, high and low humidity, exposure to pollutants, corrosion, hail, high winds, sandstorms and other natural forces. State-of-the-art solar panels are typically comprised of silicon wafers interconnected into a string of 36 and mounted into sandwich structure, as depicted in Figure 1.

Tin Oxide (SnO ₂) Coating
3mm Glass (Low-Iron)
Compliant polymer, e.g. poly ethylene-co-vinyl acetate (EVA)
Interconnected silicon wafers (36)
Compliant polymer (EVA)
Glass

Figure 1 - Schematic representation of a typical PV module.

In some cases, the back sheets of EVA and glass are replaced with sheets of EVA and Tedlar. It is noteworthy and for purposes of clarity, a cell is a semiconductor device that converts sunlight into direct current (DC) electricity and PV modules consist of PV cell circuits sealed in an environmentally protective laminate, the fundamental building block of PV systems. PV panels include one or more PV modules assembled as a pre-wired, field-installable unit and a PV array is the complete power-generating unit, consisting of any number of PV modules and panels as illustrated in Figure 2.

From Cell to Array

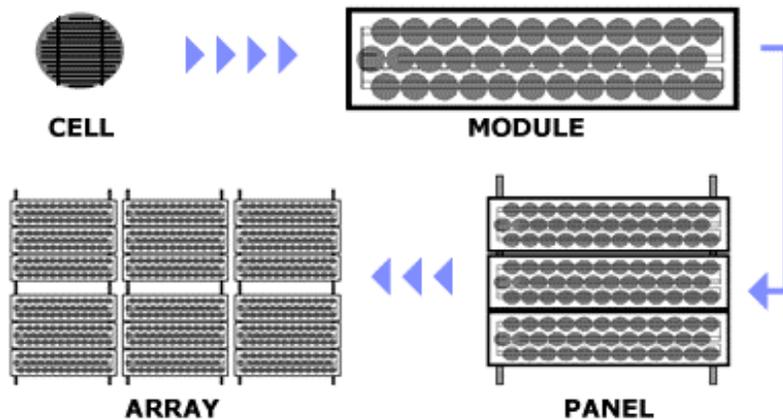


Figure 2. Schematic of the construction process for a solar array

The ultimate objective is a low-density material that can achieve an operational service life threshold of 30 years with no more than 3% transmission degradation over the 400 nm to 2000 nm region of the electromagnetic spectrum. In light of this, the proposed polymers are selected from a family of block copolymers of perfluorinated polyimide and fluorosilicones with varying ratios of F: Si. These novel copolymers designed to maintain a high degree of transmissivity over the solar spectrum used by solar cells. The structure of the imide groups is selected on the basis of its ability to tolerate UV radiation. It may be also necessary to evaluate covalent bonding of the organic layer to the cell, perhaps utilizing a silane coupling reaction. The copolymer film will be cross-linked with cross-linking density varying continuously from a very low value for the layer immediately next to the cell, to a medium to high value for the top layer. This outermost hard, tough layer is expected to most radiation stable, while the soft layer in contact with the cell will serve to isolate the cell from mechanical stress.

In essence, we are proposing a generic technology development program leading to a rationale design of cell bonding, taking into environmental requirements and performance limitations of the active device. Substantial cost and weight savings may result from the application of thinner polymer films that possess superior radiation resistance, mechanical properties, combined with enhanced thermal stability. The rationale behind the proposed approach is that carbon to fluorine bonds and aromatic structures are more stable in environment; polyimides are more stable than silicones and Teflon is the most stable polymer.

Thin films of perfluorinated polyimides are optically transparent in 400 – 2000 nm region of the electromagnetic spectrum. This means that they are excellent candidates for encapsulating multi-junction solar cells of the type envisioned in the present application.

Anticipated Public Benefits

If the project is successful and is carried over into Phases II and III, the technical, economic, social and environmental benefits will be significant. It is reasonable to assume that more energy in the form of sunlight strikes Earth in one hour than all of the energy consumed by humans in an entire year. The alternatives to fossil fuels are nuclear, wind, hydroelectric, biomass and geothermal. As of this writing, global energy usage is on the order of 13 terawatts, 85% of which is generated by burning fossil fuels. The implications for climate change are obvious and it is clear that the sun is the only viable and renewable source capable of quenching man's thirst for energy. One route to assist fabricators of photovoltaic arrays to tap into this vast energy resource inexpensively is a light weight polymeric encapsulant with the optical and thermal properties suitable for multi-junction solar cells.

The proposed project will also be useful to researchers in their quest for new materials and strategies for designing photovoltaic systems that convert sunlight into electricity. In addition to exploring new methods for reducing the cost of solar cells based on silicon, the traditional photovoltaic material, scientists have been experimenting with other semiconductors, inorganic nano-crystals, organic polymers, and a host of other light-sensitive materials. The

point is that the proposed copolymers will be suitable for encapsulating present and future photovoltaic materials.

All groups in the commercial and governmental sectors will benefit from the projected results because of the anticipated decrease in the amount of fossil fuels used to generate electricity. Specifically, manufacturers and users of PV arrays and the U.S. DOE's Solar America Initiative will no doubt benefit because an effective encapsulant for broadband multifunctional solar cells will assist in accelerating the development of advanced PV systems. The proposed project will contribute to the goal of making PV cost competitive with electrical power generated by the burning of fossil fuels by 2015.

The resultant project is a dilute solution of a polymer in an organic solvent to permit the uniform deposition of thin films directly on the solar cells. The probability that this product will be marketable is quite high, if the optical and environmental properties can be demonstrated early in Phase I. This is based on prior work conducted for photovoltaic arrays for application in space. The significance of the market is obvious based on the amount of sheet glass that is currently used and the amount projected as the cost of solar cells becomes low enough so that solar energy is competitive with energy generated by burning fossil fuels in an environment where the public is aware of global warming.

Technical Objectives

The goal is to develop synthetic and processing techniques for a series of elastomeric copolymers of perfluorinated polyimides and fluorosilicones, and evaluate them for use as thin film encapsulants for photovoltaic modules to be used in photovoltaic arrays.

Specific technical objectives for the Phase I effort are to:

1. Prepare and characterize block copolymers in a preliminary screening program, while developing a set of selection criteria for candidates for a detailed experimental study, including additional syntheses and characterizations.
2. Synthesize suitable block copolymers and characterize their key physical properties controlling performance, such as elastic moduli, thermal stability, optical absorption coefficient over the 400 – 2000 nm range, as well as briefly assess their charging and flammability characteristics, and their long term durability.
3. Optimize the synthetic procedure;
4. Evaluate a limited number of laminates comprising of: experimental copolymer/cell/polyimide to demonstrate feasibility, and for delivery to the DOE.
5. Prepare the final report.

In pursuit of the primary goal of demonstrating feasibility of the concept, Phase I will answer the following questions:

- A. What is the optimal composition for the lower layer of the copolymer?
- B. What is the optimal composition for the top layer of the copolymer?
- C. What is the extinction coefficient of the combined layers between 400 nm and 2000 nm?

- D. What are the glass transition temperatures of both layers of the copolymer?
- E. What is the stress-strain relationship of the copolymer layers?
- G. What is the peel adhesion of the bottom layer of copolymer to the solar cell?
- H. What is the percent transmissivity of the optimal copolymer?
- I. What is the UV radiation resistance of the laminate?
- J. What is the thermal stability of the laminate?
- K. What is the resistance of the laminate to humidity cycling?

Phase I Work Plan

Phase I Work Plan Outline

1) Scope

The work during Phase I involves: (a) synthesis, characterization, optimization and evaluation of several copolymers of perfluorinated polyimides and fluorosilicones for use as optical encapsulants solar cells and (b) the demonstration of the feasibility of the concept.

2) Task Outline

The work during Phase I is organized along four main tasks as delineated above in the Technical Objectives. These tasks are: Preliminary screening; synthesis and characterization; optimization; evaluation; and reporting.

TASK 1. PRELIMINARY SCREENING OF COPOLYMERS

During this task, we will prepare and characterize several copolymers in order to select and identify suitable candidates for further study. The principal objective is to prepare optically transparent copolymers using well established procedures for preparing siloxane polyimides (1-3). All substrates will be spin coated with the experimental adhesives in order to prepare films with uniform thickness. Radiation resistance testing will be performed on 25 μm thick films.

1.1 Development of Selection Criteria

The four major selection criteria are optical, mechanical, thermal, and charging characteristics of the candidate materials. As mentioned before, flammability and degassing characteristics will also have to be taken into account. In addition, vacuum UV radiation stability is a primary concern. These criteria were initially used to select the class of elastomers of the present proposal. The selection criteria will be further used to define the range of copolymer compositions and cross-linked densities, which will be evaluated in Phase I. A design of experiment approach will be used to predict the composition and cross-link density ranges within the targeted copolymer family in order to achieve the desired glass transition temperature (T_g) and optical absorption characteristics.

1.2 Preparation of Copolymers

The first polysiloxane copolymers will be prepared using essentially the same procedure described in the patent literature (1-3), except that perfluorinated dianhydrides, diamines, and an amine terminated polysiloxane will be the starting materials. The polysiloxane diamine

with pendant vinyl groups is prepared using the following procedure:

1.2.1 Preparation of polysiloxane

A monofunctional silane, 1, 3-bis (3-aminopropyl) 1, 1, 3, 3,-tetramethyl disiloxane, is reacted with that amount of octamethyl cyclotetramethyl disiloxane, capable of yielding x moles of dimethyl siloxy groups and also with that amount of 1,3,5, 7-tetravinylcyclotetrasiloxane capable of yielding y moles of methyl vinyl siloxy groups, where $x + y = n$.

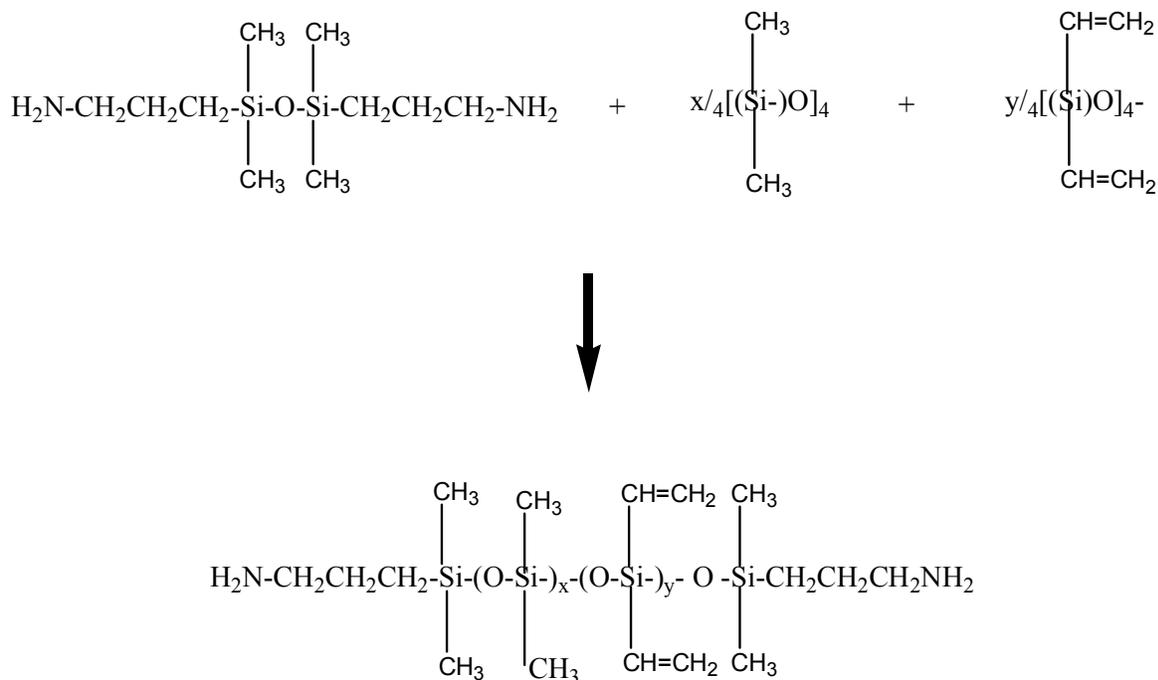


Figure 3 - Chemical processes involved in the synthesis of amine terminated polysiloxane

A mixture of the disiloxane and tetramers is combined with a trace amount of potassium hydroxide in a four neck flask fitted with a reflux condenser, an argon inlet and a mechanical stirrer. The flask is immersed in a silicone oil bath at 85°C to heat the reaction mixture. The chemical reaction is complete when the viscosity of the reaction mixture reaches a constant level or when the solution changes from a multiphase mixture to a single phase solution. At the end of the reaction, the catalyst is neutralized and the mixture is cooled, filtered and percentage of functional groups determined by titration.

1.2.2 Preparation of polysiloxane perfluoroimide

Because the method of preparing the amino terminated polysiloxane is an equilibrium reaction, a Gaussian distribution of molecular weights results. Consequently, in the

preparation of the polyimide siloxane, the lower molecular weight diamines will react first with the perfluorinated dianhydride. Hence, we propose to gradually add the dianhydride to the solution of the polysiloxane diamine over an extended period of time at room temperature and then commence refluxing after all the dianhydride has reacted. At the end of the polycondensation reaction, we will add a small amount of the dianhydride and continue the refluxing until no unreacted polysiloxane diamine is present. Any unreacted dianhydride will be removed during the isolation and rigorous purification of the polymer. Oxidation of the unreacted polysiloxane diamine typically results in the formation of colored species. When the diamine is removed or fully reacted, the optical transparency of the cross-linked elastomeric siloxane polyimide is equivalent to that of DC-93500.

A four neck flask equipped with mechanical stirrer, nitrogen or argon inlet, thermometer, condenser coupled to a Dean Stark trap is charged with: a mixture of the disiloxane, methyl tetramers having (0.01 mole) of amine, zone refined or recrystallized 10 F (or 2F) dianhydride, and 450 grams monochlorobenzene. A catalytic amount of (0.15 gram) of para-toluenesulfonic acid is added and the entire reaction mixture is stirred and heated to reflux under nitrogen such that the water formed during cyclization is removed azeotropically with the solvent. The evolution of water ceases after two hours, but refluxing is allowed to continue for an additional three hours. After cooling, the polymer is isolated by precipitation in methanol and dried under reduced pressure in a vacuum oven.

This elastomeric copolymer is designed for application as the bottom layer of the adhesive in direct contact with the solar cell. And in our effort to increase the F:Si ratio, we will gradually replace some of the polysiloxane with each of the following: 14 F diamine and 4 F diamines (para- and meta-), which are depicted in Figures 4 - 6 below.

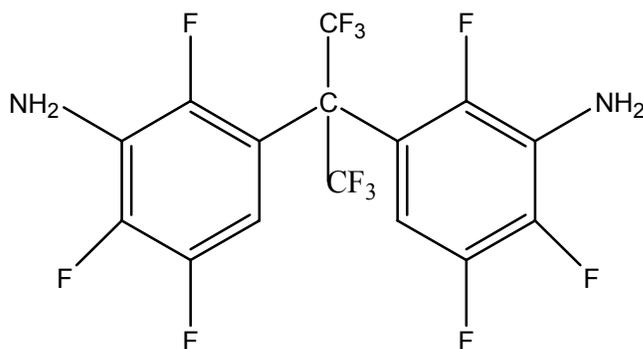


Figure 4. Molecular Structure of 14F Diamine

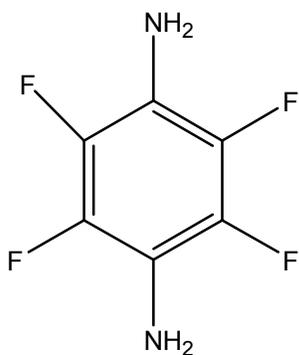


Figure 5. Chemical structure of para- 4F Diamine

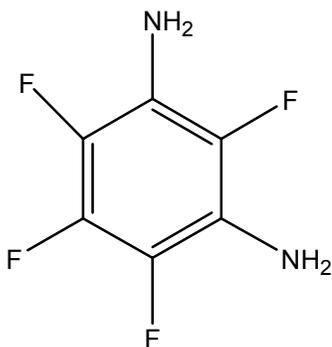


Figure 6. Structure of ortho- 4F Diamine

These are selected to further increase the toughness and radiation stability of the adhesive; they will be used to coat the top layer, so that they are in direct contact with the cover glass.

Further, a tetramer with trifluoromethyl groups will be used to prepare other polysiloxane diamines which will be reacted with purified perfluorinated dianhydrides (10 F and 4 F) and subsequently with appropriate concentrations of purified 14 F and 4 F diamines. Purification is necessary to increase the optical transparency of the adhesive. A transmissivity of 0.95 is the goal.

The chemical structures of the dianhydride raw materials are shown in Figures 7 and 8.

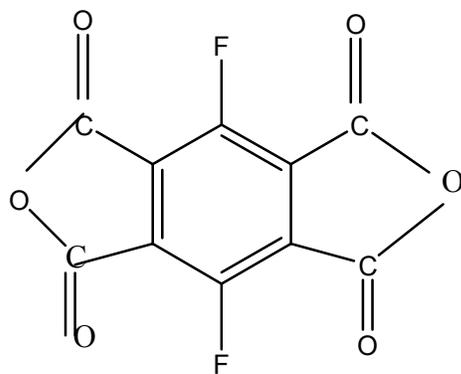


Figure 7. Chemical structure of 2F Dianhydride

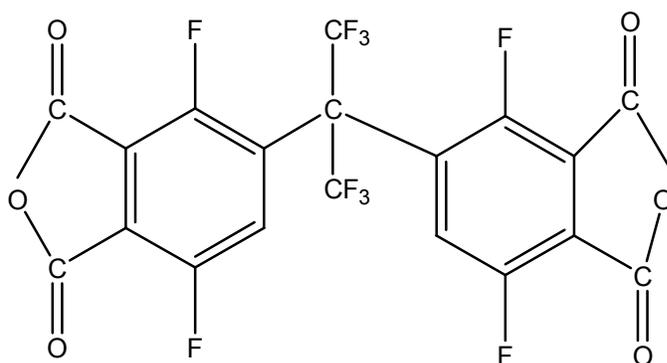


Figure 8. Structure of 10 F Dianhydride

The chemical reactions leading to the synthesis of the experimental polyimide siloxane are given in Figure 9.

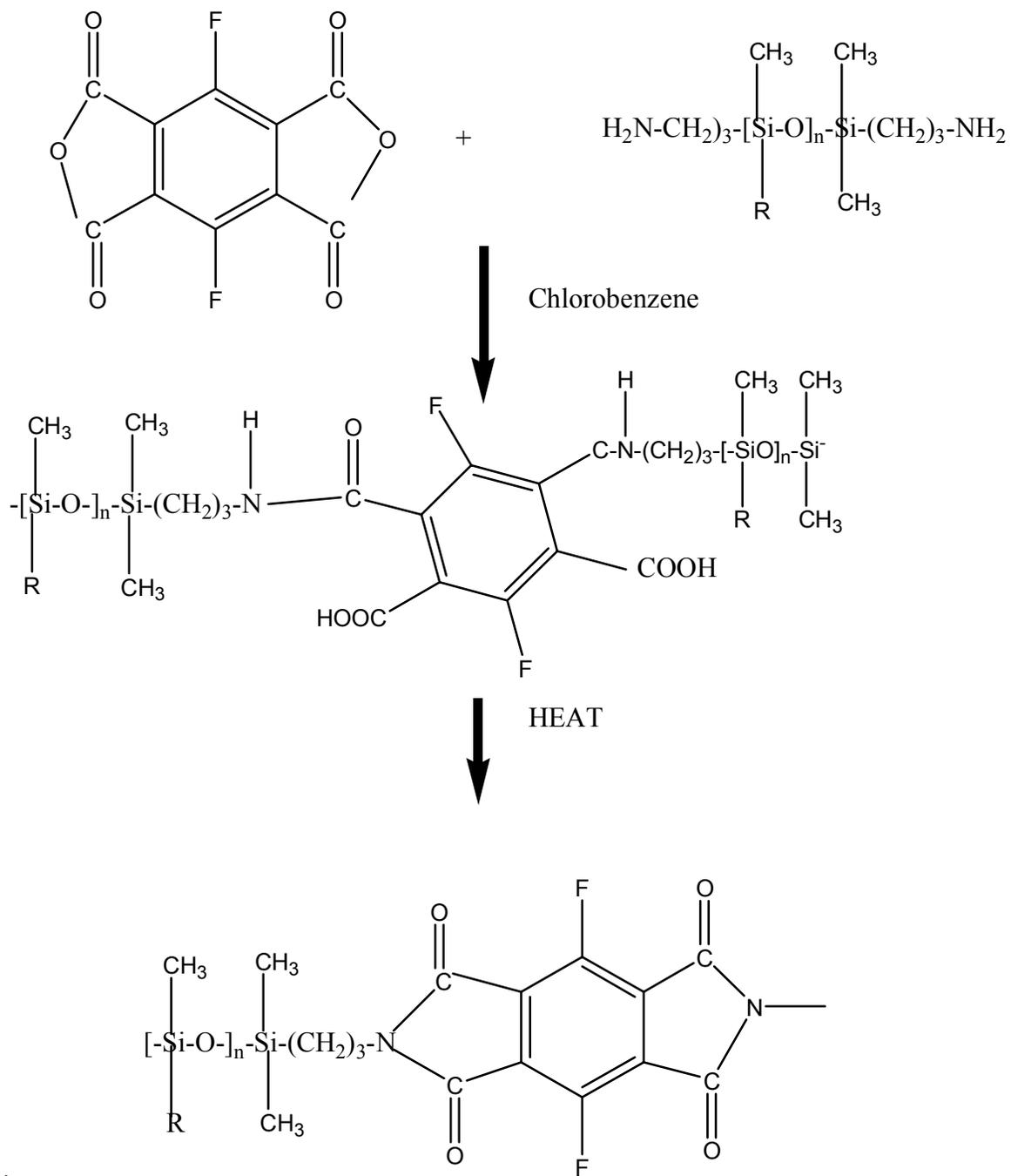


Figure 9. Chemical reactions involved in the synthesis of perfluorinated polyimide siloxane

1.3 Characterization of Copolymers

The objective of this sub-task is to identify and select those copolymers that are suitable for further experimental study in subsequent tasks. Accordingly, we will determine the following:

1.3.1 *UV-Visible spectra*

The extinction coefficients between 400 nm and 900 nm will be determined here on optically transparent candidates in the proposer's laboratory.

1.3.2 *Elemental analyses*

Small samples will be sent to Galbraith Laboratories for determination of %C, %H, %Si, %F. The results will be used in a database so that we can identify the optimal ratio of F:Si.

1.3.3 *FTIR*

The infrared spectra of thin films on sodium chloride cells will be recorded in the proposer's laboratory.

1.3.4 *Molecular weight*

Selected samples will be sent to DuPont Analytical Solutions for gel permeation chromatography of dilute solutions in THF.

1.3.5 *Thermal Analysis*

DSC and TGA analyses of promising samples will be conducted by DuPont Analytical Solutions.

TASK 2. SYNTHESIS AND CHARACTERIZATION

The primary objective of this task is to synthesize and characterize the most optically transparent copolymers identified in the preliminary screening program. The synthetic procedure will be fine tuned further, including more intensive purification of starting materials, including solvents. The purpose is to further increase the optical transparency of the copolymers. After the results of the synthesis can be duplicated, the most suitable copolymers will be characterized and evaluated.

Following synthesis, the films will be evaluated for application as encapsulants for solar cells. Performance characteristics, such as optical transmission over the wavelength range 400 nm to 2000 nm will be measured by DuPont Analytical Solutions. Tensile stress-strain response up to break will be measured over a selected temperature range by Plastic Testing Laboratories. Dynamic response will be measured on a TMA apparatus by DuPont. Polydimethyl silicones are known to have a crystal transition at or near room temperature. It is our intent to suppress this phase transition in the experimental copolymers, if it exists. The adhesive bond strength will be determined through peel tests, which will be performed as a function of temperature. Laminates will be subjected to a selected number of thermal cycles, followed by a peel test, in order to determine if the adhesive bond strength is significantly altered by thermal cycling. No attempt will be made to deduce long term performance from these data; the sole use of these data will be to determine feasibility of the concept.

Thermal properties will be estimated from TGA and DSC measurements conducted by DuPont. But charging, flammability and degassing characteristics will be deferred till Phase II.

It is perhaps instructive to state that we ultimately want to determine if the optical and mechanical properties of the best copolymers can be retained after exposure to ultraviolet (1 sun air-mass-zero equivalent) for 1000 hours between 30-40°C at atmospheric pressure. And that thermal cycling in a terrestrial environment involves the temperature range of -20°C to 100°C.

But the first requirement is an optically transparent copolymer. Hence, we will only evaluate optically clear reaction products. Those copolymers which exhibit optical clarity in the visible region will be sent to DuPont Analytical Solutions for determination of a plot of extinction coefficient versus wavelength between 400 nm and 2000 nm.

TASK 3. OPTIMIZATION

During this task, the synthetic procedure that yields an optically transparent polyimide silicone will be refined to improve the optical clarity of thin (25, 50 and 75 µm) films reproducibly. This will entail using the optimal ratio of Fluorine to Silicon and other parameters identified in the preliminary screening program.

TASK 4. EVALUATION

Those systems which possess the necessary transmissivity will be rigorously evaluated here. Accordingly, the following will be determined during this task:

- 4.1 Optical Properties
- 4.2 Adhesion
- 4.3 Humidity Cycling
- 4.4 Thermal Cycling
- 4.5 Thermal Stability under a vacuum
- 4.6 Radiation Resistance:

The performance of PV modules and arrays is generally rated according to their maximum DC power output (watts) under Standard Test Conditions (STC). Standard Test Conditions are defined by a module (cell) operating temperature of 25° C (77° F), and incident solar irradiant level of 1000 W/m² and under Air Mass 1.5 spectral distribution. Since these conditions are not always typical of how PV modules and arrays operate in the field, actual performance is usually 85 to 90 percent of the STC rating.

(UL), qualification testing will be deferred till Phase II.

TASK 5. PREPARATION OF FINAL REPORT

At the conclusion of the experimental work, we will prepare a final report with a discussion

of all results and test data, including estimates of technical feasibility.

Performance Schedule

The relevant milestones are answers to the questions posed in the Technical Objective section of the proposal. It is not possible to give precise dates at the present time because of the iterative nature of the applied research plan. Table 1, however, is a tentative schedule for reaching significant milestones during Phase I.

Table 1 Milestone Schedule

<u>Milestone</u>	<u>Months following SOW</u>
Identification of the optimal composition of lower layer of polymer.	5
Identification of the optimal composition of top layer of polymer	6
Identification of suitable ratio of F:Si	5
Successful preparation of an optical transparent perfluorinated polyimide siloxane with a transmissivity of 0.95	6
Characterization of optical properties of the copolymers	6
Characterization of stress-strain relationship of the copolymers	4

Related Research or R&D

We are unaware of any published research to encapsulate multi-junction solar cells with perfluorinated polyimides.

References

1. Berger, Ade; "Siloxane-Containing Polymers," U.S. Patent 4,395,527, assigned to M&T Chemicals Inc., July 26, 1983.
2. Holub, Fred F.; Scotia, N.Y.; "Polysiloxane-imides and their Production," U.S. Patent 3,325,450, assigned to General Electric Company, June 13, 1967.
3. Fessler, William; "Method for Making Polyimide Block Copolymers," U.S. Patent 3,736,290, May 29, 1973.

Principal Investigator and other Key Personnel

Dr. Ronald W. Gumbs will serve as principal investigator on the project. He has the requisite experience and training to synthesize the proposed materials using raw materials that are commercially available.

Facilities/Equipment

RWG Corporation has a modern research facility in East Brunswick, NJ with 1,400 square feet of laboratory space and the option to lease more space as the need arises. The firm maintains a library, machine shop and a glass-blowing capability at this location. Equipment

includes all standard equipment, including two custom-built 6' fume hoods, for chemical synthesis and characterization.

This facility meets all environmental laws and regulations of federal, New Jersey, and local Governments for the following groupings: airborne emissions, waterborne effluents, external radiation levels, outdoor noise, solid and bulk waste disposal practices, and handling and storage of toxic and hazardous materials.

The firm has a Master Services Agreement with DuPont Analytical Solutions providing access to a comprehensive analytical laboratory when the need arises. Typically, a request for quotation is made and samples are subsequently submitted. The laboratory offers a full range of services from routine testing to complex analytical problem-solving. It is an organization of experienced professionals with a strong support staff and world-class capabilities presently being used by the proposer. A request for a quote is followed with an estimate. If funds are available, the sample is forwarded to DuPont with a purchase order.

The firm also has working and informal arrangements with the Materials Testing Laboratory of NJIT, Plastic Testing Laboratories, and Galbraith Laboratories.

Additional specific major pieces of equipment owned by the proposing firm and located in its laboratory in East. Brunswick, include:

1. A complete electrochemical research system based on an EG & G Princeton Applied Research (PARC) Model 273 Potentiostat/Galvanostat and Houston Instruments Model 2200GW X-Y recorder.
2. Spectra-Physics Model GCR-11-3 Nd:YAG ns pulsed laser with 2nd, 3rd harmonic generation and pulse compression, associated optics, positioners, two Scientech Model 36-5002 digital power meters, an Antel Optronics Model AR-S1-C custom large-area picosecond photodetector, mounted on a Newport precision optical table. A 2.5 - 7.0 ns, 200 mJ (@ 532 nm) laser pulse repeating at 1 - 15 Hz is available.
3. Instron Model 4201 Universal Testing Machine; a state-of-the-art instrument for measuring mechanical properties of polymeric materials.
4. Perkin-Elmer Model Lambda 3B automated UV-Vis. Spectrophotometer; also used in conjunction with PARC 273 for spectro-electrochemistry.
5. Perkin-Elmer Model 1615 FT-IR.
6. Tektronix oscilloscopes: Model 2210, digital storage, Model DCA 602, pico-second digital storage.
7. Optical train and laser/optic instruments incl. Newport Model C-2001-65ML 65 mW Ar ion laser with acousto-optic (Isomet) modulation, Newport Model M-877 200 ps photodetector, Oriel Model 66165 150 W Xe source, Model 77250 monochromators, associated wavelength controllers, drives, optics, 3-axis positioners. Used for spectroelectrochemical, polymer studies.
8. Denton Vacuum Model 502A high vacuum thermal evaporation system (for thin film semiconductor, metal and other depositions).
9. Resistivity/conductivity and electrical test instrumentation: Signatone Model S301-4

- 4-point resistivity probe interfaced to Keithley Model 617 electrometer, Keithley Model 220 current source; Keithley Model 197A digital multimeter.
10. Integrated Technologies, Inc. Model P6204 Spin Coater.
 11. Power supplies for Electropolymerization: Micronta Dual Tracking and Vector-Viz WP-773A, associated bulk (1 L) synthesis cells.
 12. Precision Instruments vacuum pumps and high-vacuum line system.
 13. Ovens/Furnaces: Labline IV and Thermolyne F21100 tube furnace (to 1200°C).
 14. Large capacity LabLine Imperial controlled-temperature system.
 15. Ultraviolet light sources for polymerization initiation, related functions.
 16. U.S. Stoneware Ball and Jar Mill, Model No. 753 RM/V.
 17. Brookfield Viscometer
 18. Dymax Model 1200 Focused Beam UV-curing system

Consultants and Subcontractors

This grant application does not contain any collaboration with a research institution and there is no involvement of consultants or subcontractors in the planning or research stage.