tics of the substrate. After driving off the solvent by gentle heating and/or by use of a vacuum, the coated substrate is packed into an inert tube with openings at each end. (The dried precious-metal coating is somewhat sensitive to light; the dried coated substrate should be handled accordingly and stored in the dark.)

The coated substrate is held in place with small quantities of inert wadding (i.e., borosilicate glass wool). A gas suction pump is attached to one end of the tube, and the air or other gas suspected to contain hydrazine vapor is drawn through the tube at a specified pumping rate for an amount of time sufficient to obtain a sufficient chemical change (and thus an observable color change) in the coating material. A semiquantitative relationship between the degree of chemical change and the quantity of vapor sampled can be established from observations of intensities of color changes and/or areas of color change in tests on similarly prepared substrates and tubes using known concentrations of hydrazine vapors.

In experiments, tubes containing $KAuCl_4$-coated substrates prepared as described above were exposed to 40-liter flows of air containing, variously, hydrazine, monomethylhydrazine, or unsymmetrical dimethylhydrazine at concentrations of the order of 0.01 ppm. These exposures caused the colors of the substrates to change from yellow to various purplish colors and, in one case, to black.

No such color changes were observed upon exposure of the $KAuCl_4$-coated substrates to flows of air that contained other gases (ammonia, isopropyl alcohol, NO_2, and H_2). Whether or not other precious-metal coating materials could be used as color-change indicators of these or other nonhydrazine gases remains to be determined.

This work was done by Louis A. Dee and Benjamin Greene of Allied-Signal Aerospace Co. for **Johnson Space Center**. *For further information, contact the Johnson Commercial Technology Office at (281) 483-3809.*
MSC-22870

Amplifying Electrochemical Indicators

Reporter compounds can be formulated for high sensitivity and miniaturization of sensor units.

Ames Research Center, Moffett Field, California

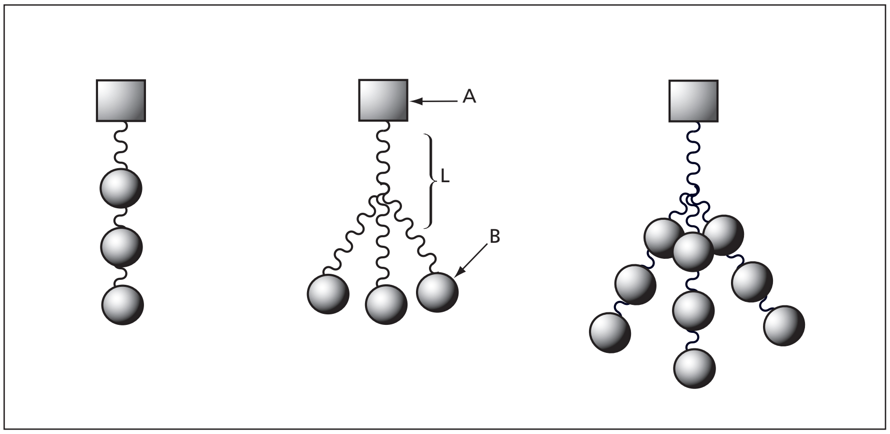
Dendrimeric reporter compounds have been invented for use in sensing and amplifying electrochemical signals from molecular recognition events that involve many chemical and biological entities. These reporter compounds can be formulated to target specific molecules or molecular recognition events. They can also be formulated to be, variously, hydrophilic or amphiphilic so that they are suitable for use at interfaces between (1) aqueous solutions and (2) electrodes connected to external signal-processing electronic circuits. The invention of these reporter compounds is expected to enable the development of highly miniaturized, low-power-consumption, relatively inexpensive, mass-producible sensor units for diverse applications, including diagnoses of infectious and genetic diseases, testing for environmental bacterial contamination, forensic investigations, and detection of biological warfare agents.

The multiple functionality of a reporter compound of this type is achieved through integration of a variety of chemical moieties into each molecule. The structure and composition of such a molecule is depicted schematically in the figure and represented by the general formula ALB_n. As used here, A signifies a targeting group, L signifies a linking group, and B signifies an active group.

The targeting group (A) can include nucleic-acid intercalators or other organic functional subgroups. It is designed to interact directly with a targeted molecule or molecular recognition event; that is to say, it is designed to bring itself and the rest of the reporter molecule into the vicinity of the target. Hence, the collective effect of the targeting groups of multiple reporter molecules is to concentrate the reporter compound in the region of the target compound or molecular recognition events that one seeks to detect.

An active group (B) is, more specifically, either (1) electroactive in a manner that enables detection of an electrochemical signal or (2) hydrophilic to enhance solubility. It is preferable that the number (n) of B groups exceed 1. The linking group (L) comprises two moieties: (1) a linker between the targeting (A) group and the B groups and (2) an amplifying moiety, through which the B groups are connected in series, parallel, or a combination of series and parallel connections in a dendritic structure.

The active (B) groups can also be characterized as indicator groups because these are the ones that generate the desired electronic sensory signals. Because they are linked to the targeting group, the active groups are concentrated in the vicinity of the target, and the probability that each will generate a signal is correspondingly increased. The multiple active groups, connected together in the dendritic molecular structure, contribute to an aggregate signal much greater than that generated by a single-indicator reporter molecule. Depending upon the specific formulation of a reporter molecule according the invention, the primary signal could be as little as two



A **Reporter Compound** according to the invention can have any of a wide variety of dendritic structures. The A, B, and L groups contribute synergistically to the overall effect of generating a highly amplified primary electrochemical sensory signal.

times or more than a thousand times as great as that generated by a single-indicator reporter molecule. By increasing signal-to-noise ratios relative to those available from prior reporter compounds, the invention of these reporter compounds can be expected to facilitate the detection of very small amounts of target compounds — for example, particular genes in blood samples.

This work was done by Wenhong Fan, Jun Li, and Jie Han of **Ames Research Center**. *Further information is contained in a TSP (see page 1).*

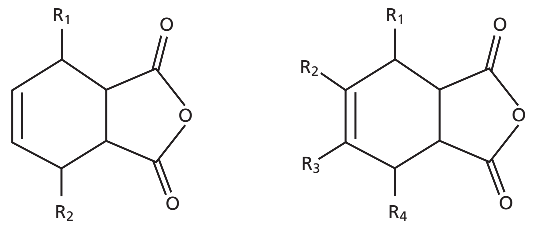
Inquiries concerning rights for the commercial use of this invention should be addressed to the Patent Counsel, Ames Research Center, (650) 604-5104. Refer to ARC-14908-1.

Better End-Cap Processing for Oxidation-Resistant Polyimides

Cross-linking in an inert atmosphere (as opposed to air) yields better results.

John H. Glenn Research Center, Cleveland, Ohio

A class of end-cap compounds that increase the thermo-oxidative stability of polyimides of the polymerization of monomeric reactants (PMR) type has been extended. In addition, an improved processing protocol for this class of end-cap compounds has been invented.



PREVIOUS VERSION

PRESENT (EXTENDED) VERSION

End Caps of These Molecular Structures are alternatives to previously reported end caps for increasing the thermo-oxidative stability of polyimides. R1 through R4 can be any of a variety of substituents (for example, alkyl, alkoxy, aryl, halogen, or nitro), the inclusion of which reduces the cross-linking temperature.

The class of end-cap compounds was described in "End Caps for More Thermo-Oxidative Stability in Polyimides" (LEW-17012), *NASA Tech Briefs*, Vol. 25, No. 10 (October 2001), page 32. To recapitulate: PMR polyimides are often used as matrix resins of high-temperature-resistant composite materials. These end-cap compounds are intended to supplant the norbornene end cap (NE) compound that, heretofore, has served to limit molecular weights during oligomerization and, at high temperatures, to form cross-links that become parts of stable network molecular structures. NE has been important to processability of high-temperature resins because (1) in limiting molecular weights, it enables resins to flow more readily for processing and (2) it does not give off volatile byproducts during final cure and, therefore, enables the production of void-free composite parts. However, with respect to ability of addition polymers to resist oxidation at high temperature, NE has been a "weak link." Consequently, for example, in order to enable norbornene-end-capped polyimide matrices to last for lifetimes up to 1,000 hours, it is necessary to limit their use temperatures to ≤315 °C.

Like NE, these end caps are also subject to oxidation at high temperatures, but they oxidize in a different manner, such that the long-term stability of a polymer made with one of these end caps exceeds the long-term stability of the corresponding polymer made with NE. Hence, use temperatures and/or lifetimes can be increased. The approach taken in formulating these end caps is to seek derivatives that preserve the desirable processing properties of NE while exploiting one of the modes of the thermo-oxidative degradation of the nadic end cap in such a way as to retard the overall thermo-oxidative degradation of the affected polymers.

The figure depicts the generic molecular structures of the prior version and the present extended version of this class of end caps. Each end cap is a 1,2,3,6-tetrahydrophthalic anhydride, substituted in such a way as to lower the cross-linking temperature. The end cap maintains its stability during imidization (at 200 °C) and cross-linking.

If the imidization is carried out in air, then the end cap subsequently aromatizes in competition with cross-linking. This aromatization is undesirable. Therefore, the improved processing protocol specifies that the process be carried out in an inert atmosphere, wherein cross-linking is the predominant, if not the exclusive, reaction path. Following cross-linking, the end cap is spontaneously converted, upon aging in air, to a thermally stable capping group.

This work was done by Mary Ann B. Meador of **Glenn Research Center** *and Aryeh A. Frimer of Bar Ilan University, Israel. Further information is contained in a TSP (see page 1).*

Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Commercial Technology Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-17429.