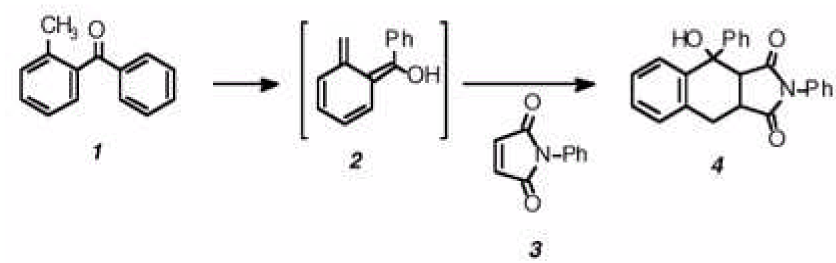
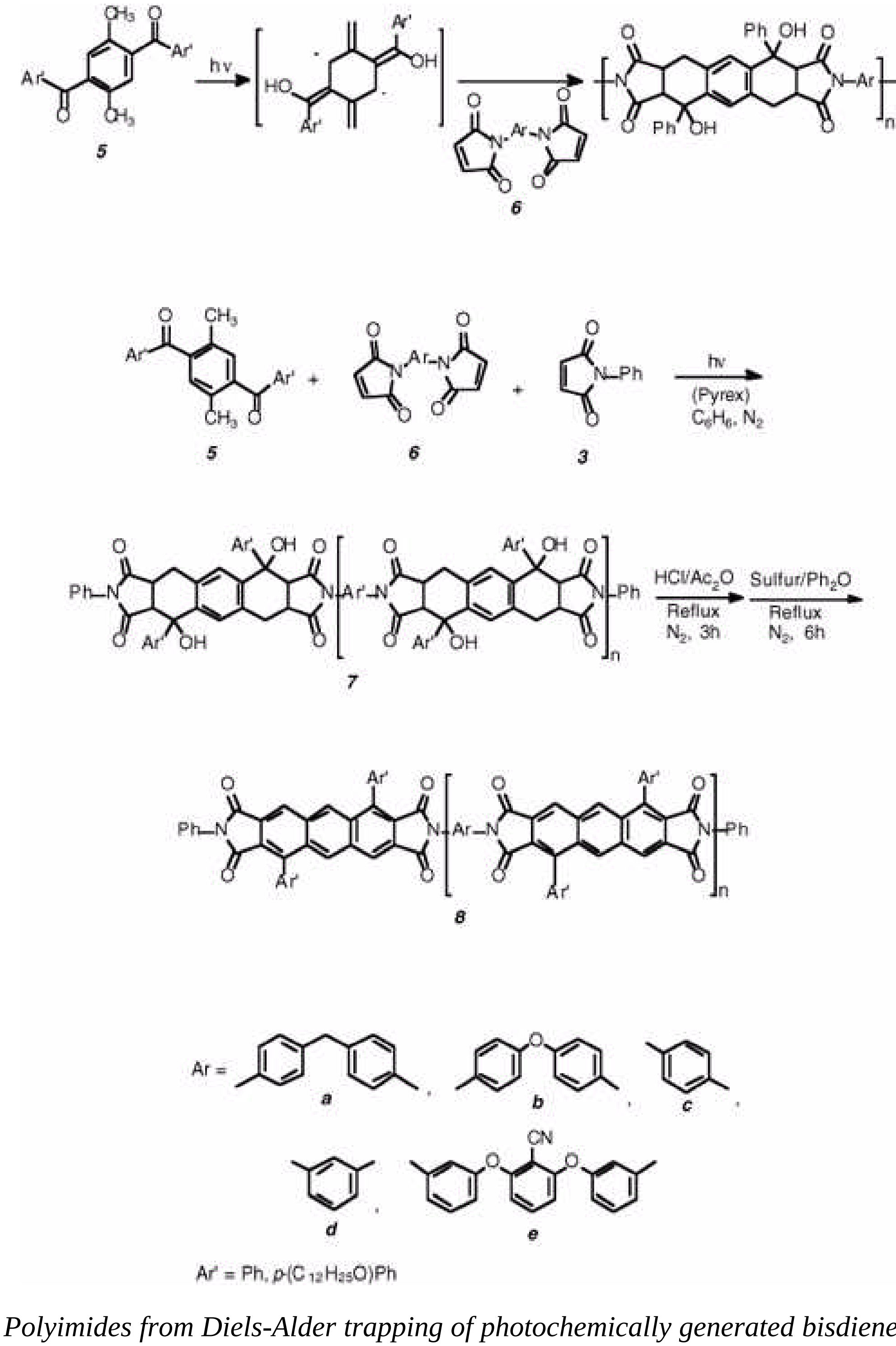
Novel Ultraviolet-Light-Curable Polyimides

Polyimides have found broad application in fiber-reinforced composites for aerospace components and as thin films for electronics packaging. Typical routes to processing these materials require temperatures above 200 °C. As a result, tooling costs for fabricating components from these composites can be quite high. Recent efforts within the Polymers Branch at the NASA Lewis Research Center have been aimed at developing radiation-curable (with light or electron beams) polyimides. Such materials may enable the processing of polymers and composites at or near room temperature, leading to reduced tooling requirements and costs.



*Generation and trapping of photoenol, **2,** from o-methylbenzophenone, **1**.*

A new Diels-Alder route to polyimides has been developed that employs ultraviolet light (UV), rather than heat, to effect polymerization. This approach, which can be carried out at room temperature, is based on a well-known photochemical reaction--the photoenolization of *o*-methylphenyl ketones. Irradiation of *o*-methylphenyl ketones, such as ***1*** in the preceding figure, with UV wavelengths above 300 nm produces a photoenol, ***2***. This photoenol is unstable, but it persists long enough to undergo Diels-Alder reactions with good dienophiles, such as maleimide, ***3***. By utilizing a diketone, such as 2,5-dibenzoyl-*p*-xylene, ***5***, and a bismalemide, ***6***, this chemistry has been used to make a number of polyimides, ***7*** (see the following figure).



Polyimides from Diels-Alder trapping of photochemically generated bisdienes.

These polyimides have glass-transition temperatures as high as 300 °C and have modest stabilities in both air and nitrogen. Onsets of decomposition, measured by thermal gravimetric analysis, were as high as 400 °C in air and 450 °C in nitrogen. Higher glass-transition temperatures and onsets of decomposition can be obtained by conversion of polyimide ***7*** into polyimide ***8*** through acid-catalyzed dehydration followed by dehydrogenation (as shown in the second figure). These polyimides have glass-transition temperatures as high as 330 °C and onsets of decomposition as high as 550 °C in air and 525 °C in nitrogen.

This chemistry has been demonstrated in solution (benzene or cyclohexanone). However, it should be easily adapted to achieve solid-state (solvent-free) curing, making it well-suited for thin-film applications (coatings, electronics packaging, and photonic and optical materials).

This new UV curing process could offer several advantages over other methods of preparing polyimides. UV-cured films should undergo less shrinkage during cure than thermally cured films. UV curing would also be useful for processing polyimides containing thermally sensitive groups or additives, such as photonic materials. Current efforts are aimed at modifying this chemistry to enable electron-beam curing of polyimides and polyimide-based composites for aeropropulsion and reusable launch vehicle applications.

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