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## Communications

### Phthalocyanine Glasses

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Monomeric phthalocyanine compounds with an isotropic glassy morphology are a new and previously unreported class of optical materials with a unique and useful combination of mechanical and processing properties. In this communication we present a molecular design and synthesis methodology for the preparation of materials with these properties.

For a design strategy, the key considerations are utilization of irregular molecular symmetry to inhibit or suppress molecular order and crystallization and incorporation of hydrogen-bonding functional groups to promote intermolecular attractions in a noncrystalline matrix. These features are incorporated onto a phthalocyanine molecule at the ring periphery to counteract the strong tendency of the phthalocyanine structure to form ordered aggregates.<sup>1</sup> The macroscopic results of such features should be a nonscattering nonbirefringent optical transparency due to a lack of long-range order and a glass transition temperature that allows processing at elevated temperatures (100–200 °C). A very useful feature of monomeric glasses is a low viscosity above the glass transition temperature which promotes facile processing and material repair.

The synthesis of a glassy phthalocyanine is presented in Scheme 1. The K<sub>2</sub>CO<sub>3</sub>-catalyzed nucleophilic nitro

displacement<sup>2</sup> of 4-nitrophthalonitrile by 3-aminophenol results in a 4-(3-aminophenoxy)phthalonitrile precursor which is converted to the phenyl glycidyl ether-amine adduct. This adduct is then cyclotetramerized in the presence of hydroquinone as reducing agent<sup>3</sup> to form the product, tetrakis(3-(*N,N*-bis(3-phenoxy-2-hydroxypropyl ether)amino)phenoxy)phthalocyanine,<sup>4</sup> abbreviated H<sub>2</sub>-Pc(PGE3Ap)<sub>4</sub>.

This peripherally substituted phthalocyanine product has several features of irregular symmetry which inhibit crystallization and/or long-range molecular order. These include a mixed geometrical isomer substitution at either of the outer benzo positions of the phthalocyanine structure, a meta as opposed to para substitution of the aminophenoxy group, and a diastereomeric relationship between the two asymmetric carbons in the amine-epoxy adduct structure. Intermolecular hydrogen bonding from the amine-epoxy adduct structure restricts molecular motion, thereby raising the glass transition temperature. The flexible ether linkages positioned at the phthalocyanine macrocycle periphery and within the aliphatic epoxy adduct contribute to a well-defined glass transition and a lowered viscosity above it.

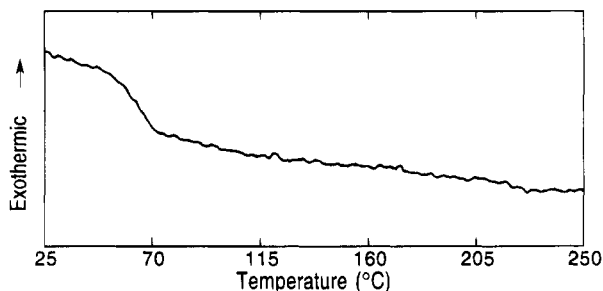
As physical evidence of a glassy phthalocyanine state, the following observations are reported. The DSC thermogram displays a well-defined glass transition temperature at 65 °C and no melting or other detectable phase transitions (Figure 1). A dark-field optical microscope observation detected no birefringence when a phthalocyanine film was cast from solution and thermally cycled above its glass transition temperature. At

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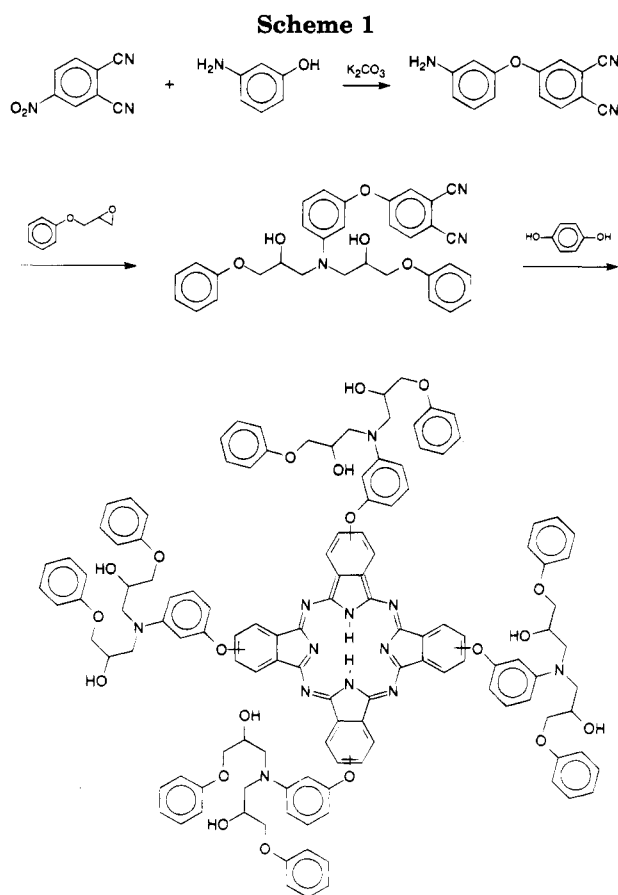
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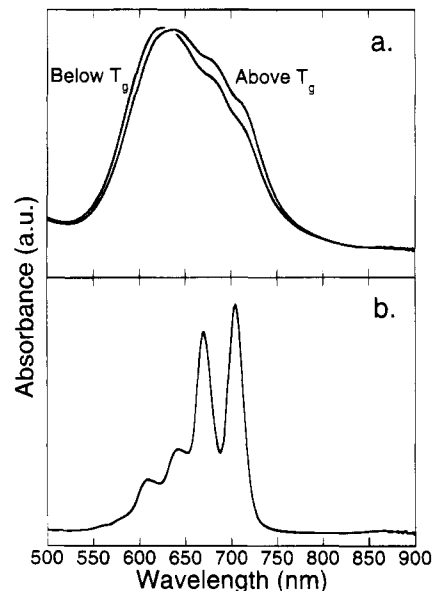
(4) Elemental analysis: calculated 71.7% C, 5.5% H, 7.8% N; found 71.2% C, 5.6% H, 7.6% N. <sup>1</sup>H NMR (DMSO) δ -4.0 (broad, cavity NH), 3.4–4.4 (broad/unresolved, aliphatic CH), 5.1–5.5 (broad/unresolved, OH), 6.2–7.8 ppm (broad/unresolved complex multiplet, aromatic CH). OH and NH resonances were confirmed by deuterium exchange.



**Figure 1.** DSC thermogram for  $\text{H}_2\text{Pc}(\text{PGE3Ap})_4$ . The only phase transition observed for this material is a distinct glass transition at 65 °C.



the molecular level, when a cofacial phthalocyanine dimer or a higher aggregate forms, the  $\pi-\pi^*$  transition (Q-band) is perturbed. In the electronic spectrum the monomer Q-band is converted to a broadened and blue-shifted transition corresponding to an associated species.<sup>1</sup> Comparative spectra of this phthalocyanine in a dilute  $\text{CHCl}_3$  solution ( $10^{-6}$  M) and as a solid-state glassy thin film are shown in Figure 2. The spectrum of the dilute solution corresponds to that for an isolated phthalocyanine monomer,<sup>1</sup> whereas the spectrum of the film displays characteristics of significant cofacial association. At temperatures above the glass transition, the solid-state Q-band displays a very slight spectroscopic shift in the direction of the monomer, but the spectral line shape of the associated species predomi-



**Figure 2.** Comparison of  $\text{H}_2\text{Pc}(\text{PGE3Ap})_4$  electronic spectra in the Q-band region for (a) a thin film cast from solution on a glass microscope slide and (b) a dilute solution ( $10^{-6}$  M in  $\text{CHCl}_3$ ). The film was heated above the glass transition temperature and the spectrum collected during cooling (161–154 °C). The spectrum of the film below the glass transition temperature (65 °C) was collected at 55 °C and remained unchanged down to room temperature.

nates. The molecular design of this example successfully promotes a glassy morphology but does not appear to suppress the strong tendency of the phthalocyanine molecules to associate cofacially. This short-range molecular order is not sufficient to cause visually observable scattering or macroscopic birefringence. If a transition from a short-range order to long-range order is considered to be the scattering of visible light or the optical magnification limit for observable birefringence, this would occur at a domain size on the order of 500 nm. Such a domain might accommodate 50–100 phthalocyanine molecules. The example described here, while not free of oligomeric association, is isotropic down to this threshold.

While much past and current research has been directed at ordered phthalocyanine morphologies (solid- and liquid-crystal structures),<sup>5,6</sup> we believe the example described here represents a new class of phthalocyanine materials uniquely characterized by an absence of long-range molecular order. The structure–property effects of various substitutions and isomer structures will be reported in detail in the near future.

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