

Novel Glass-Forming Organic Materials. 2. Structure and Fluorescence of Pyrene- and Carbazole-Containing Cyclohexane, Bicyclooctene, and Adamantane

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A series of novel glass-forming organic materials consisting of pyrenyl and carbazolyl groups attached to cyclohexane with a 1-axial-2-equatorial configuration, bicyclo[2.2.2]oct-7-ene with an all-exo configuration, and adamantane were synthesized and characterized. On the basis of proton NMR spectra, it was found that the rotation of pendant pyrenyl and carbazolyl groups is restricted in the bicyclic system presumably because of steric hindrance in the all-exo configuration. In contrast, free rotation was found to prevail in cyclohexane- and adamantane-based systems. Fluorescence spectra gathered in solution at room temperature show evidence exclusively for intramolecular excimer formation in pyrene-containing compounds up to a concentration of 10^{-4} M. On the contrary, carbazole-containing compounds are not prone to excimer formation in the concentration range 10^{-6} – 10^{-3} M, presumably because of the more stringent requirements of interchromophoric distance and orientation. Although both pyrene and carbazole are highly crystalline on their own, attachment to cyclic, bicyclic, and tricyclic central cores was found to contribute to an ease of vitrification of the hybrid systems with a T_g ranging from 43 to 132 °C. Moreover, the quenched glasses of all seven model systems were found to possess morphological stability in view of the absence of recrystallization upon heating from 0 to 200 °C at a heating rate ranging from 0.2 to 20 °C/min. Morphological stability was further supported by the absence of recrystallization upon prolonged thermal annealing at temperatures above T_g .

I. Introduction

In recent years organic materials have received increasing attention in both linear and nonlinear optical applications because of the tremendous versatility in molecular design to optimize relevant properties and the relative ease with which synthesis and processing can be accomplished. There are basically two approaches to functional organic materials, polymeric and low molar mass in structure, that are capable of vitrification. Empirically, low molar mass materials are desirable from a processing standpoint, especially in practical applications where thin films with a high degree of uniformity are required. Although numerous low molar mass glass-formers have been reported,^{1–5} it remains a challenging task to design functional materials capable of forming morphologically stable, organic glasses. The term "morphological stability" is used to describe the resistance of a glass or melt to thermally activated recrystallization. In a recent series of papers,^{6–9} we

have reported a variety of organic materials based on a new molecular design approach in which two structural constituents are involved: functional moieties and volume-excluding cores. The term "volume-excluding core" was used to describe an aliphatic ring system to which functional moieties are covalently attached. The basic idea is for these two structural elements to present a volume-excluding effect on each other as a means to prevent recrystallization from the melt of the combined entity.

In the present work, we explored low molar mass, glass-forming materials containing pyrenyl and carbazolyl groups that are typical electron- and hole-transport moiety, respectively, for electroluminescent^{10,11} and other^{12,13} applications. The ability to integrate these two functional moieties into a glass-forming molecular

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