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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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environment, resulting in readily processable materials, will enhance their potential for practical applications. To be presented in this communication are novel chemical systems and their glass-forming ability as determined by the ability to vitrify on cooling from melt and the stability against recrystallization on heating from below glass-transition temperature up to crystalline melting point. The tendency for excimer formation as determined by the inherent nature of the chromophore and the stereochemistry as imposed by the central core will also be elucidated with fluorescence characteristics in dilute solutions.

II. Experimental Section

Reagents and Chemicals. All solvents and reagents were used as received from the Aldrich Chemical Company or VWR Scientific with the following exceptions: Tetrahydrofuran (99%) was dried by refluxing over sodium in the presence of benzophenone until blue and then distilled. Prior to their use, 1-pyrenylmethanol and *N*-ethylcarbazole were recrystallized from methanol and *n*-hexane, respectively. The synthesis of 1,3,5,7-adamantanetetracarboxylic acid chloride was accomplished by photochemical chlorocarbonylation of 1,3-adamantanedicarboxylic acid in an excess of oxalyl chloride as reported previously.[14]

Material Synthesis. *Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic and trans-1,3,5-cyclohexanetricarboxylic acids:* Hydrolysis of bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride in boiling water followed by recrystallization from water yielded bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid. Proton NMR (in DMSO-d_6), δ 11.92 (s, 4H, carboxylic acid), δ 6.06 (d, 2H, alkene), δ 2.99 [s, 6H, overlap of bridgehead (2H) and methine (4H) signals]. A procedure reported by Steiz[15] was followed to convert commercially available *cis*-1,3,5-cyclohexanetricarboxylic acid into a trans isomer with a 1-axial 2-equatorial configuration.

3-(N-Carbazolyl)propanol: 3-bromo-1-propanol was protected with the tetrahydropyranyl group following previously reported procedures.[16] Carbazole was reacted with the THP-protected 3-bromo-1-propanol followed immediately by cleavage of the protecting group to yield the precursor alcohol. The procedure is as follows: carbazole (4.99 g, 29.8 mmol), THP-protected 3-bromo-1-propanol (7.38 g, 33.1 mmol), Cs_2CO_3 (19.5 g, 59.8 mmol), and KI (0.5 g, 3 mmol) were stirred with 50 mL of anhydrous DMF under dry nitrogen. The slurry was heated to 85−90 °C for 12 h. The reaction mixture was shaken with 100 mL of diethyl ether and 100 mL of water, and the layers were separated. The organic layer was washed with water (100 mL × 3) and evaporated to dryness. Ethanol (50 mL) and pyridinium *p*-toluenesulfonate (2 g, 8 mmol) were added to the solid residue. A temperature of about 60 °C was maintained for 15 h followed by workup with diethyl ether and water. The crude product was purified by flash chromatography on silica gel using methylene chloride/acetone (40:1) as the eluent, yielding 3-(*N*-carbazolyl)propanol (2.99 g, 44%). Proton NMR (in $CDCl_3$): δ 7.25−8.12 [m, 8H, aromatic], 4.50 [t, 2H, $CH_2C\mathbf{H_2}N$], 3.64 [t, 2H, $HOC\mathbf{H_2}CH_2$], 2.15 [m, 2H, $CH_2C\mathbf{H_2}CH_2$], and 1.48 [s, 1H, O**H**].

Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid, tetrakis-[4-(1-pyrenyl)butyl] ester: All seven ester products were made by reacting a precursor alcohol with *trans*-1,3,5-cyclohexanetricarboxylic acid, *exo*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid, and 1,3,5,7-adamantanetetracarboxylic acid chloride following the general procedures as accomplished previously.[7−9] The procedures involved in synthesis and purification are illustrated as follows. Under a dry nitrogen atmosphere, 4-(1-pyrenyl)butanol (0.545 g, 1.986 mmol), *exo*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid (0.141 g, 0.496 mmol), and triphenylphosphine (0.696 g, 2.66 mmol) were dissolved in dry tetrahydrofuran (8 mL) and dry DMF (4 mL). Diethylazodicarboxylate (0.44 mL, 2.8 mmol) was then added dropwise over 15 min. About 2 h later, the reaction mixture was shaken with diethyl ether (100 mL) and water (100 mL). The organic layer was dried over anhydrous $MgSO_4$ before evaporating the solvent to dryness. The crude product was obtained by flash chromatography on silica gel using methylene chloride/acetone (40:1) as the eluent. It was further purified by a gradient elution with methylene chloride/hexane (3:1) gradually changed to methylene chloride/acetone (5:1) as the eluent to obtain the pure product (0.24 g, 37%). Proton NMR (in $CDCl_3$) δ 8.14−7.72 [m, 36 H, aromatic], 6.37 [m, 2 H, $\mathbf{H}C{=}C\mathbf{H}$], 3.98 [m, 4 H, $COOC\mathbf{H_A}H_BCH_2$], 3.87 [m, 4 H, $COOCH_A\mathbf{H_B}CH_2$], 3.26 [s, 2 H, bridgehead], 3.18 [t, 8 H, $COOCH_2CH_2CH_2C\mathbf{H_2}$], 2.90 [s, 4 H, $C\mathbf{H}COO$], 1.70 [m, 8 H, $COOCH_AH_BCH_2C\mathbf{H_2}CH_2$], 1.62 [m, 8 H, $COOCH_AH_BC\mathbf{H_2}CH_2$-$CH_2$].

Characterization Techniques. A Hitachi high-performance liquid chromatography (HPLC) system comprising an L-2000 metering pump and an L-4200 UV−vis absorbance detector equipped with an LiChrosorb column (RP-18, 10 μm) was employed to determine the number of components and purity of the intermediates and products. The purity levels of all final products were found to be better than 99% based on HPLC analysis. Chemical structures were elucidated with elemental analysis (performed by Oneida Research Services, Inc. in Whitesboro, NY), FTIR (Nicolet 20 SXC), and proton NMR (QE-300, GE) spectroscopic techniques. A Perkin-Elmer MPF-66 fluorescence spectrophotometer with a xenon lamp was used to acquire emission spectra in dilute solutions at room temperature. Thermal transition temperatures were determined by differential scanning calorimetry (DSC, Perkin-Elmer DSC-7) with a continuous nitrogen purge at 20 mL/min. A heating rate of 20 °C/min in DSC experiments was normally employed to gather a thermogram unless noted otherwise.

III. Results and Discussion

Pyrene- and carbazole-containing cyclohexane, bicyclooctene, and adamantane systems synthesized for the present study are as depicted in Figure 1. The chemical structures are consistent with the elemental analysis and proton NMR spectral data compiled in ref 17. To facilitate our interpretation of NMR spectra in what follows, the spectrum of 1-pyrenylmethanol in $CDCl_3$ was gathered. The singlet at δ 5.39 is attributed to the methylene protons, thus precluding the possibility of long-range coupling with the ortho aromatic proton. The 1-axial 2-equatorial configuration on the cyclohexane ring was confirmed by comparing the NMR spectral region from δ 1.6 to 3.0, as illustrated in Figure 2 for compound I, characteristic of protons on the cyclohexane ring as elucidated previously.[18] The two singlets at δ 5.71 and 5.79 with integrations in the ratio 2:1 are clearly associated with the methylene protons between the pyrenyl and carboxylate groups in the equatorial and axial positions, respectively. In view of the fact that the more viscous DMSO was needed as a solvent for gathering the proton NMR spectrum of compound III, it was decided that the spectrum should also be taken of compound I in DMSO-d_6. Again the three methylene groups appear as two singlets at δ 5.70 and 5.74 with integrations in the ratio 2−1 corresponding to equatorial and axial positions, indicating free rotation of pyrenyl

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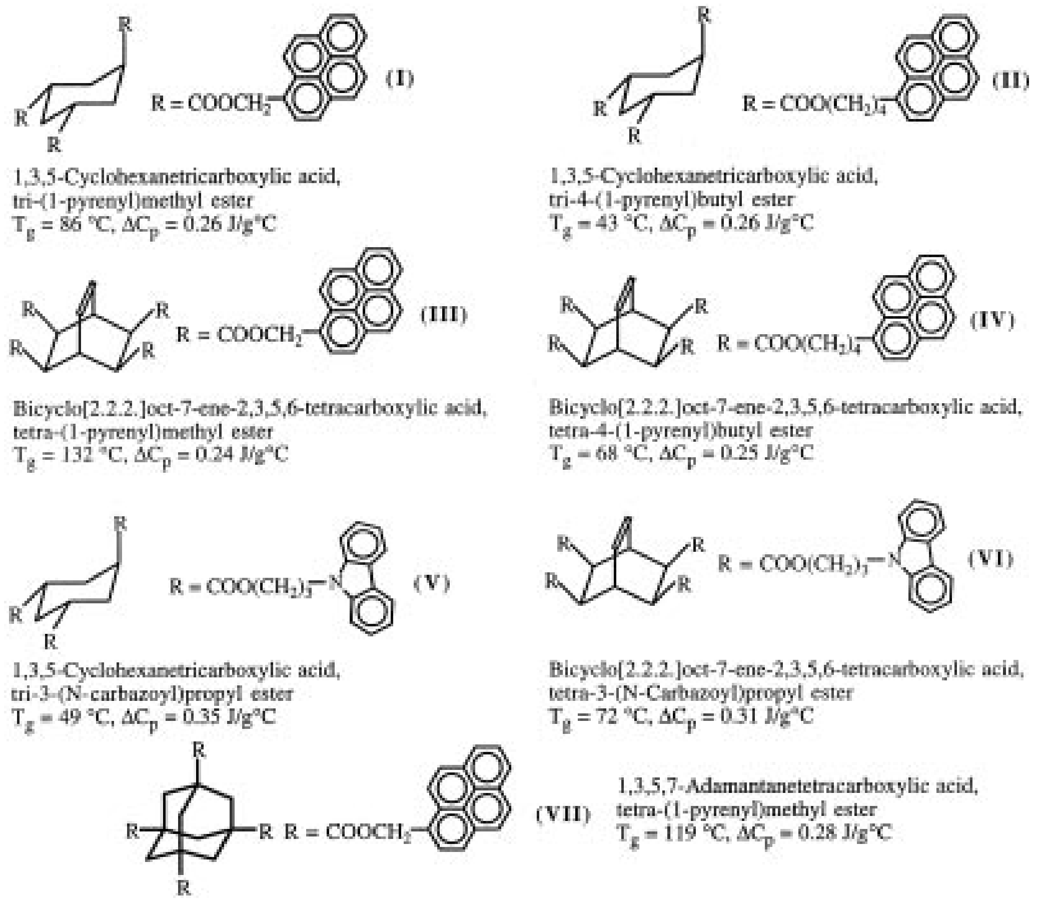

Figure 1. Chemical structures of compounds I–VII accompanied by thermal transition data, T_g and ΔC_p, determined for quenched glasses by DSC at a heating rate of 20 °C/min; samples preheated to 200 °C followed by quenching at −200 °C/min to −60 °C.

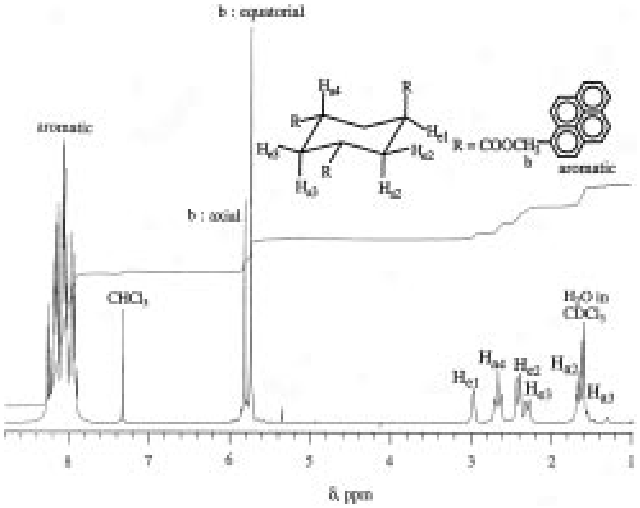

Figure 2. Proton NMR spectrum, 300 MHz, for compound I in $CDCl_3$.

rings. Likewise, the fact that a singlet at δ 5.75 was observed in compound VII indicates free rotation of pyrenyl rings attached to adamantane. If the rotation of pyrenyl rings were hindered, each singlet should be split into a doublet as observed in compound III to be described below.

As we have reported recently,[6] bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid prepared from its dianhydride assumes an all-exo configuration, and the ester synthesis under mild conditions of the Mitsunobu reaction is not expected to alter the stereochemistry. As a consequence, one might anticipate that the methylene group connecting the pyrenyl to carboxylate group, as in compound III, should give rise to a singlet. As shown in Figure 3, this methylene group is responsible for two doublets at δ 5.33 and 5.56 with a coupling constant, J_{AB} = 12.3 Hz, suggesting the magnetic nonequivalence of the two protons, which is believed to arise from the restricted rotation by pyrenyl rings in an all-exo configuration. This conclusion was reached based on the observation that the ethyl ester of the same *all-exo*-tetracarboxylic acid, in which the two methylene protons between the methyl and carboxylate group appear as a

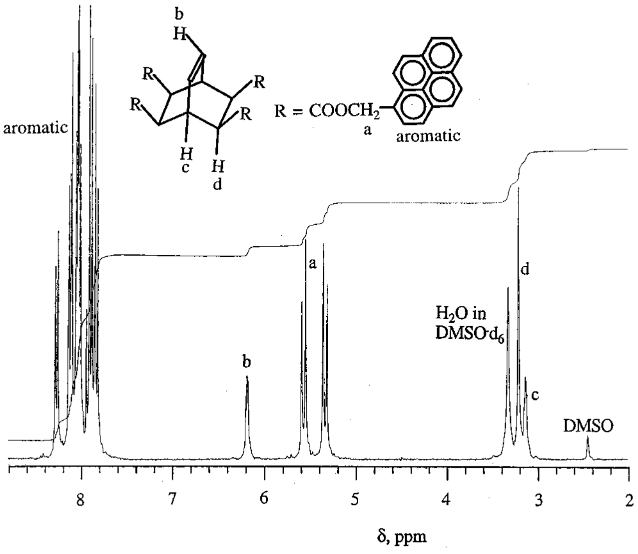

Figure 3. Proton NMR spectrum, 300 MHz, for compound III in DMSO-d_6.

quartet at δ 4.09,[19] indicating the magnetic equivalence of these two protons. The two methylene protons next to the carboxylate group in compound IV were also found to be magnetically nonequivalent in their appearance as two multiplets at δ 3.98 and 3.87. As a result of irradiation at δ 1.62 (identified for $COOCH_AH_BC\mathbf{H_2}$-CH_2CH_2), these two multiplets were found to collapse into two doublets with $J_{AB} = 10.5$ Hz, resembling the two at δ 5.33 and 5.56 observed in compound III. In short, pyrenyl groups attached to bicyclooctene ring in an all-exo configuration are subject to hindered rotation. In contrast, as pyrenyl rings are attached to cyclohexane in a 1-axial 2-equatorial configuration, they seem to be capable of free rotation. These same observations were also made in compounds V and VI, in which carbazolyl groups are connected to the two ring systems via a propylene spacer. Specifically, in compound V the methylene protons next to the carboxylate group yield two triplets at δ 4.15 and 4.20 with integrations in the ratio 2:1, signifying a 2-equatorial 1-axial configuration. In compound VI with an all-exo configuration, the same methylene protons appear as two overlapping multiplets centered at δ 4.03, instead of a triplet as expected on the basis of a neighboring methylene group at δ 2.12 (identified for $COOCH_AH_BC\mathbf{H_2}CH_2$). Upon irradiation at δ 2.12, the multiplet at δ 4.03 was found to collapse into two doublets with $J_{AB} = 11.1$ Hz. Thus, the ability of the pendant rings to undergo free rotation is determined primarily by the stereochemistry imposed by the central core.

Let us look into the implication of the rotation of pendant pyrenyl and carbazolyl groups, as revealed by proton NMR spectroscopy, on excimer formation as detected by fluorescence spectroscopy. Shown in Figure 4 are the fluorescence spectra, with an excitation wavelength, λ_{ex}, at 344 nm, of 1-pyrenylmethanol as well as compounds I–IV and VII in methylene chloride at concentrations ranging from 5×10^{-6} to 1×10^{-4} M (in pyrenyl groups). The spectrum of 1-pyrenylmethanol is attributed to emission from monomeric pyrene,[20] indicating the absence of chromophoric interaction leading to excimer formation. On the other hand, there is an increasing trend in excimer formation between pendant pyrenyl groups as they are attached to the adamantane, cyclohexane, and bicyclooctene cores as evidenced by the intensity of the broad peak centered at 475 nm[20] relative to that of monomer emission. Thus, the extent of excimer formation does not seem to simply correlate with the restricted rotation of pyrenyl groups detected in the ground state. The facts that no excimer emission was observed in 1-pyrenylmethanol and that the emission spectra for all pyrene-containing compounds are independent of concentration suggest the intramolecular nature of excimer formation in compounds I–IV and VII. In contrast, pendant carbazolyl groups exhibit a different fluorescence behavior. Shown in Figure 5 are the fluorescence spectra, with a λ_{ex} of 294 nm, of compounds V and VI in addition to 3-(*N*-carbazolyl)propanol and *N*-ethylcarbazole in methylene chloride at concentrations ranging from 1×10^{-6} to 1×10^{-3} M (in carbazolyl groups) at room temperature. Practically the same set of spectra was obtained with a λ_{ex} of 320 nm. The relative intensity of the two emission peaks is determined by a significant reabsorption of the emission at 353 nm relative to that at 368 nm, as pointed out by Yokoyama et al.[21] Specifically, the peak at 353 nm diminishes to a shoulder of the peak at 368 nm at a concentration of 10^{-3} M presumably because of the overwhelming reabsorption at the shorter wavelength. Moreover, the ratio of the intensities of these two emission peaks, I_{368}/I_{353}, was found to decrease to an asymptotic value of 0.80 as expected in the limit of high dilution. The peaks at 353 and 368 nm can be attributed to emission from monomeric carbazole, as concluded by both the steady-state and dynamic fluorescence experiments involving *N*-ethylcarbazole and *trans*-1,2-dicarbazolylcyclobutane in DMF at 10^{-4} M[22] and *N*-ethylcarbazole in methylene chloride at the same concentration,[23] all performed at room temperature. On the contrary, intramolecular excimer formation was demonstrated for both 1,3-bis(*N*-carbazolyl)propane and poly(*N*-vinylcarbazole) under the same conditions.[21–24] Therefore, while the extent of intramolecular excimer formation is determined, to some extent, by the stereochemistry imposed by the central core in pyrene-containing compounds, neither intramolecular nor intermolecular excimer formation is allowed in carbazole-containing counterparts. Apparently, a more stringent stereochemical requirement will have to be met for excimer formation involving pendant carbazolyl groups.

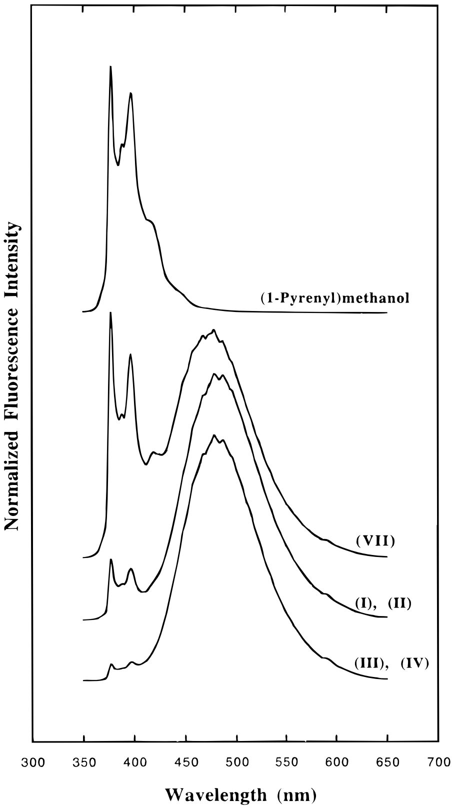

Figure 4. Fluorescence spectra (with $\lambda_{ex} = 344$ nm) of 1-pyrenylmethanol, compounds I–IV and VII in methylene chloride at room temperature and at concentrations from 5×10^{-6} to 1×10^{-4} M in pyrenyl groups.

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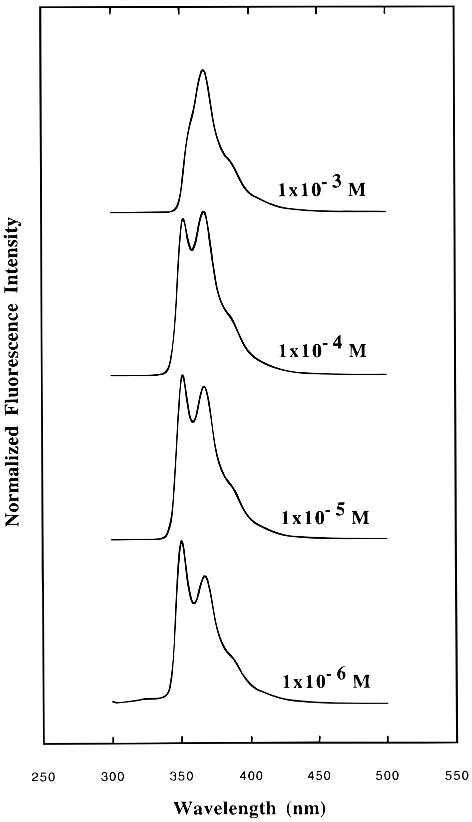

Figure 5. Fluorescence spectra (with $\lambda_{ex} = 294$ and 320 nm) of 3-(*N*-carbazolyl)propanol, *N*-ethylcarbazole, and compounds V and VI in methylene chloride at room temperature and at concentrations from 1×10^{-6} to 1×10^{-3} M in carbazolyl groups.

As indicated earlier, one of the objectives of this series of studies is to enable functional organic materials, such as highly crystalline pyrene ($T_m = 154$ °C) and carbazole ($T_m = 248$ °C), to form morphologically stable glassy films with a glass transition temperature, T_g, above the ambient. To assess the role played by the volume-excluding central core, the DSC thermograms of all three precursors to compounds I–VII, i.e. 1-pyrenylmethanol, 3-(*N*-carbazolyl)propanol, and 4-(1-pyrenyl)butanol were collected from the heating scans at 20 °C/min of the quenched samples (i.e., preheating the samples to 200 °C followed by quenching at −200 °C/min to −60 °C). Several observations were made of the DSC thermograms: (i) Quenched 1-pyrenylmethanol is crystalline with a T_m at 126 °C; (ii) quenched 3-(*N*-carbazolyl)propanol appears to be partially glassy and the amorphous melt undergoes recrystallization followed by a T_m at 104 °C; and (iii) quenched 4-(1-pyrenyl)butanol is glassy with a T_g at −12 °C and shows no evidence of recrystallization upon further heating. The DSC thermograms were then collected for compounds I–VII consisting of the three precursors attached to cyclohexane, bicyclooctene, and adamantane as the volume-excluding core. It was found that cooling of the melt of all seven model compounds resulted in vitrification without residual crystallinity. The resultant glass was then heated across T_g and up to 200 °C at a series of heating rates ranging from 0.2 to 20 °C/min in the DSC experiment as a way to assess the stability of the melt against thermally activated recrystallization. As shown in Figure 6, cyclohexane, bicyclooctene, and adamantane rings as central cores were found to promote both vitrification and morphological stability of all seven model compounds in comparison to their three precursors when subjected to identical thermal treatment. The observed values for T_g and ΔC_p, change of heat capacity across T_g, are included in Figure 1 in which chemical structures are depicted. A comparison of the thermal transition data of compounds I, III, and VII reveals that bicyclooctene gives rise to the highest T_g followed by adamantane and cyclohexane but with almost the same ΔC_p values, 0.24–0.28 J/g °C. It is also clear that a shorter spacer is capable of producing a significant elevation in T_g. An attempt was also made to quantitatively assess morphological stability through the measurement of linear spherulitic growth rate as a function of temperature, as was accomplished previously.[18] However, no observable growth rate resulted from this effort, a further indication of the stability of the melt of these materials against thermally activated crystallization.

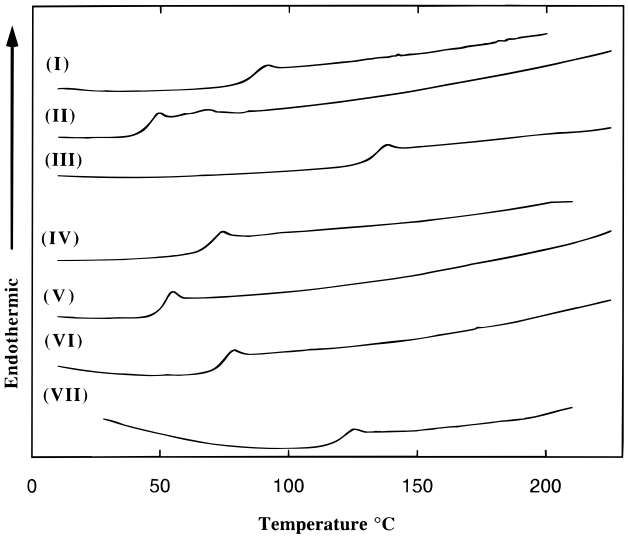

Figure 6. DSC heating scans (at 20 °C/min) of samples of compounds I–VII preheated to 200 °C followed by quenching at −200 °C/min. to −60 °C; same qualitative features were observed at a heating rate down to 0.2 °C/min.

IV. Summary

Novel organic materials were synthesized by attaching pyrenyl and carbazolyl groups to cyclohexane with a 1-axial 2-equatorial configuration, bicyclooctene with an all-exo configuration, and adamantane. The NMR spectral data suggest that the rotation of the substituent groups on the bicyclic ring is restricted presumably because of steric hindrance. In contrast, free rotation seems to prevail in the case of cyclohexane and adamantane as central cores. Fluorescence spectra in methylene chloride solutions were collected to investigate the tendency for excimer formation as affected by the nature of the chromophore and by the structure of the central core. In the case of pyrene-containing compounds, the extent of intramolecular excimer formation was found to follow the order bicyclooctene > cyclohexane > adamantane with no evidence for intermolecular excimer formation up to a concentration of 10^{-4} M. In carbazole-containing compounds, no evidence was found for excimer formation presumably because of the more stringent requirements of interchromophoric distance and orientation, that were met in poly(*N*-vinylcarbazole) and 1,3-bis(*N*-carbazolyl)propane but not in the presently investigated compound V or VI. While pyrene and carbazole are both highly crystalline, their attachment to cyclohexane and bicyclooctene rings impart glass-forming ability to the hybrid systems with a T_g ranging from 43 to 132 °C depending on the type of pendant group, central core, and the spacer length connecting the two. Furthermore, the morphological stability of all seven compounds was demonstrated by the absence of recrystallization as the quenched glasses are heated from 0 °C across their respective T_g's up to 200 °C at a heating rate ranging from 0.2 to 20 °C/min. The morphological stability was further substantiated by the absence of recrystallization from the melt upon thermal annealing at temperatures above T_g for a few days. Both the ability to form glasses and morphological stability against thermally activated crystallization are conducive to practical applications where thin glassy films are desired.

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