CHEMISTRY LETTERS, pp. 1145-1148, 1989.

Starburst Molecules for Amorphous Molecular Materials. 4,4',4''-Tris(N,N-diphenylamino)triphenylamine and 4,4',4''-Tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine

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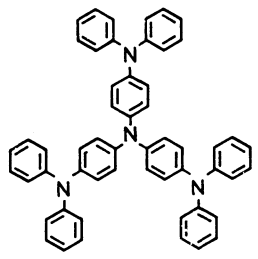
A novel class of starburst molecules for making amorphous glassy organic materials, 4,4',4''-tris(N,N-diphenylamino) triphenylamine (TDATA) and 4,4',4''-tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine (MTDATA), are synthesized and characterized. Their electrochemical and electronic properties as well as unique solid-state morphology are described.

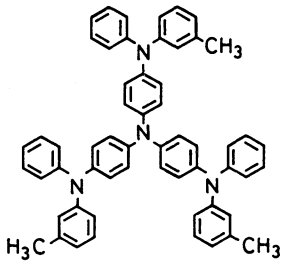
Recently, amorphous inorganic semiconductors or amorphous metals have been receiving great attention as a novel class of functional materials. Similarly amorphous organic materials consisting of small organic molecules dispersed in inert polymeric binders have also been studied from both fundamental and practical viewpoints.[1,2] However, only limited classes of molecular materials form stable amorphous glassy states at or above room temperature,[3-5] although amorphous or quasi-amorphous films of polycyclic aromatic hydrocarbons are known to be formed by vapor deposition onto a substrate maintained at low temperature.[6]

We report here the synthesis and properties of a novel class of starburst molecules consisting of a fully conjugated π-electron system, 4,4',4''-tris(N,N-diphenylamino)triphenylamine (TDATA) and 4,4',4''-tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine (MTDATA), for making amorphous molecular materials. These compounds are shown to form stable amorphous glassy states above room temperature by differential scanning calorimetry and X-ray diffraction. They are characterized by very low oxidation potentials and higher conductivities than ordinary organic compounds as well as by film-forming capability. They function as

photoactive materials for photovoltaic devices.



TDATA



MTDATA

The new compounds, TDATA and MTDATA, were synthesized in 17 and 19% yields, respectively, by a two-step reaction pathway starting from triphenylamine: the triiodonation of triphenylamine with potassium iodide and potassium iodate in acetic acid at 85 °C for 5 h under nitrogen, followed by the Ullmann reaction with the corresponding amines in the presence of copper and potassium hydroxide at 160 °C for 6 h under nitrogen. TDATA and MTDATA were recrystallized from THF-EtOH (1:1 v/v) to give pale yellow needles, mp: 249-250 °C (TDATA), 209-210 °C (MTDATA). They were characterized by IR, UV, and mass spectra, and elemental analysis. Found: C, 86.82; H, 5.72; N, 7.42%; M^+, 746. Calcd. for $C_{54}H_{42}N_4$ (TDATA): C, 86.86; H, 5.72; N, 7.51%; M, 746. Found: C, 86.23; H, 6.30; N, 6.96%; M^+, 788. Calcd. for $C_{57}H_{48}N_4$ (MTDATA): C, 86.80; H, 6.09; N, 7.11%; M, 788.

Both TDATA and MTDATA were found to form stable amorphous glassy states with glass-transition temperatures much higher than room temperature when cooled from the melt: whereas TDATA requires rapid cooling with liquid nitrogen to form an amorphous glassy state, MTDATA spontaneously forms an amorphous glassy state regardless of the cooling rate. Figure 1 shows differential scanning calorimetry (DSC) thermograms of MTDATA. When the crystalline sample of MTDATA is heated from room temperature, an endothermic peak due to the melting is observed at 203 °C. When the sample is cooled down from the melt, it spontaneously forms a supercooled liquid state regardless of the cooling rate and then changes into an amorphous glassy state. When the amorphous glassy sample

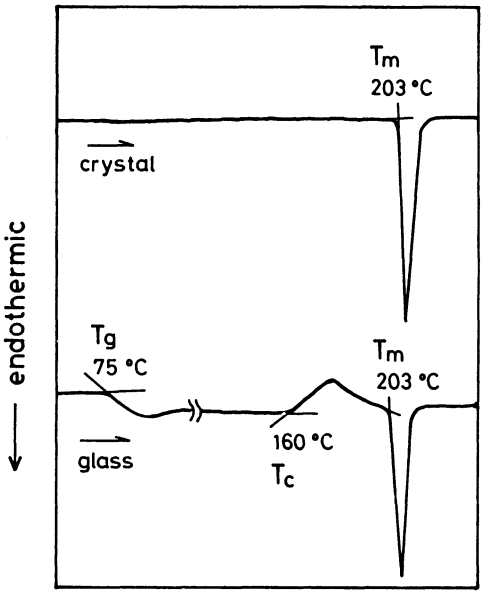


Fig. 1. DSC thermograms of MTDATA. Heating rate: 5 °C min^{-1}. Endothermic peak at T_g is enlarged compared with the other peaks for clarity reasons.

obtained by cooling down to room temperature is again heated, an endothermic phenomenon is observed at 75 °C, at which the glassy state changes into the supercooled liquid state. Then a broad exothermic peak due to the crystallization is observed around 160 °C, followed by the endothermic peak due to the melting at 203 °C. The enthalpy changes for the crystallization (ΔH = 42 kJ mol^{-1}) and for the melting (ΔH = 40 kJ mol^{-1}) were almost the same. Similar thermal properties were observed with TDATA (T_g = 89 °C) by melting the crystalline sample, followed by rapid cooling with liquid nitrogen. The X-ray diffraction patterns of the amorphous samples of TDATA and MTDATA thus formed showed no peaks characteristic of the crystals. When the amorphous glassy samples of TDATA and MTDATA were again heated above 170 °C, where crystallization occurs, characteristic peaks due to the crystals reappeared. The glassy states of these compounds are quite stable at room temperature. No crystallization has been noticed over 6 months.

The nonplanar molecular shapes of TDATA and MTDATA and the introduction of the methyl group at the meta-position of the phenyl group in MTDATA seem to prevent easy spacial reorientation of the molecules, and consequently crystallization, when cooled from the melt, and thus favoring the formation of the stable amorphous glassy state.

The anodic oxidation processes of these compounds are reversible ($i_{pc}/i_{pa} \simeq 1$), showing two anodic and the corresponding cathodic waves. Figure 2 shows a cyclic voltammogram of MTDATA in dichloromethane. These compounds have very low half-wave oxidation potentials, $E_{\frac{1}{2}}$ = 0.11 V and 0.06 V vs. Ag/Ag^+ (0.01 mol dm^{-3}) in dichloromethane for TDATA and MTDATA, respectively.

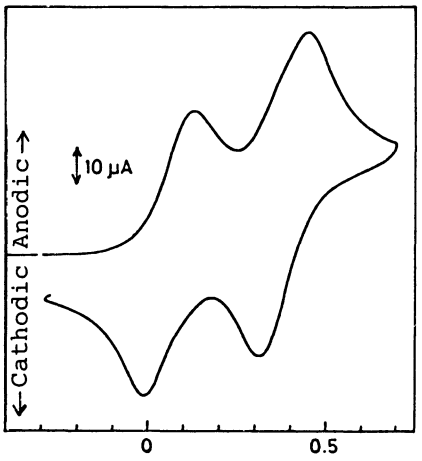


Fig. 2. Cyclic voltammogram of MTDATA in dichloromethane. Scan rate: 100 mV s^{-1}.

Although TDATA is much less soluble than MTDATA, MTDATA is soluble in tetrahydrofuran and benzene, and readily forms transparent films by a solvent cast method. Transparent amorphous films of MTDATA thus formed exhibit room-temperature conductivities of ca. 10^{-10} S cm^{-1} probably due to spontaneous partial oxidation with air oxygen because of the strong electron-donating property of MTDATA, which is higher than those for ordinary organic compounds. The activation energy for the conduction was ca. 0.38 eV. Owing to its photoconductive property coupled with a relatively low

resistivity, the amorphous film of MTDATA is expected to function as a photoactive material for photovoltaic devices, the fabrication of which using organic materials has been the subject of recent interest.[7-9] A Schottky device was fabricated using the solvent-cast MTDATA film with a thickness of ca. 8 μm, which was sandwiched between vacuum-deposited semi-transparent aluminum and Nesa glass. The dark current-voltage curve of the cell clearly showed rectification behavior with a rectification ratio of ca. 780 at ±5.0 V: this indicates that a Schottky barrier is formed at the interface between aluminum and MTDATA which acts as a p-type semiconductor. Under illumination, a photocurrent flows from aluminum to MTDATA. When the cell was illuminated through the Al electrode (transmittance: 4.8%) with 334 nm monochromatic light at 3.0 mW cm^{-2}, an open circuit voltage V_{oc} of 0.78 V, a short circuit current J_{sc} of 195 nA cm^{-2}, a fill factor of 0.29, and a conversion efficiency of 3.0 x 10^{-2}% for the transmitted monochromatic light were obtained.

The present study will enable molecular design of various starburst molecules for making amorphous molecular materials with easy processability for potential use in electronic devices.

The authors would like to thank helpful discussions with Professor Jacques Simon at ESPCI, France.

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(Received March 27, 1989)