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# Methyl-substituted Derivatives of 1,3,5-Tris(diphenylamino)benzene as a Novel Class of Amorphous Molecular Materials

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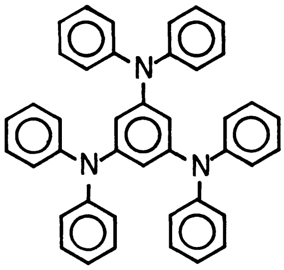
Methyl-substituted derivatives of 1,3,5-tris(diphenylamino)benzene (TDAB) are found to show unique solid-state morphology, as characterized by differential scanning calorimetry and X-ray diffraction. These compounds readily form stable amorphous glasses having glass-transition temperatures of ca. 50 °C. p-Methyl-substituted TDAB exhibits polymorphism.

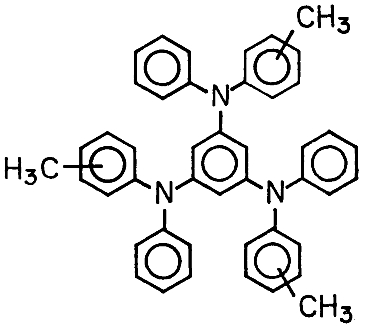
Amorphous materials are attractive for their excellent processability, flexibility, transparency, inexistence of grain boundaries, and isotropic properties. Amorphous inorganic materials and amorphous metals have recently attracted great attention as novel functional materials. With regard to amorphous organic materials, polymers are known. In addition, molecularly-doped systems, where low-molecular organic compounds are dispersed in polymers, have also received attention from both fundamental and practical viewpoints.1,2) However, little attention has been paid to low-molecular materials that form stable amorphous glasses above room temperature. Only limited classes of low-molecular organic compounds have been reported to form amorphous glasses,3-6) 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.7)

It is of interest and significance to develop photo- and electro-active amorphous molecular materials, that consist of π-electron systems and have glass-transition temperatures higher than room temperature, for use in electronic devices.

We have reported the synthesis and properties of a novel class of starburst molecules for making photo- and electro-active amorphous molecular materials, 4,4',4"-tris(diphenylamino)triphenylamine and 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine.5) In the present study, we have found that methyl-substituted derivatives of 1,3,5-tris(diphenylamino)benzene (TDAB) also constitute a novel class of amorphous molecular materials having glass-transition temperatures higher than room temperature. We report here the synthesis and unique solid-state morphology of new starburst molecules consisting of $\pi$-electron systems, TDAB and its methyl-substituted derivatives, 1,3,5-tris(3-methylphenylphenylamino)benzene (m-MTDAB) and 1,3,5-tris(4-methylphenylphenylamino)-benzene (p-MTDAB).



TDAB



m-, p-MTDAB

The new compounds, TDAB, m-MTDAB and p-MTDAB, were synthesized by the following two routes. The Ullmann reaction of 1,3,5-tris(phenylamino)-benzene with iodobenzene or the corresponding iodotoluenes in decalin at 160 °C for 6 h in the presence of copper powder and potassium hydroxide produced TDAB, m-MTDAB and p-MTDAB in yields of 63, 35 and 46%, respectively. Likewise, the Ullmann reaction of 1,3,5-triiodobenzene with the corresponding amines also gave these compounds, but the product yields were lower than those of the former reactions. The products were purified by silica-gel column chromatography, followed by recrystallization from benzene/hexane, and identified by IR, UV, NMR and mass spectroscopy, and elemental analysis.

The parent compound TDAB does not form a glassy state. It melts at 257 °C, and even when the melt sample of TDAB is rapidly cooled down with liquid nitrogen, it instantly crystallizes. By contrast, both m- and p-MTDAB are found to form readily stable amorphous glassy states. When the melt samples of m- and p-MTDAB are cooled down with liquid nitrogen or on standing in air, they form spontaneously supercooled liquid states, which change into amorphous glassy states. When the amorphous glassy samples of m- and p-MTDAB thus formed are again heated, glass-transition phenomena are observed at 49 and 58 °C, respectively. Then, crystallization takes place and melting follows. In the case of m-MTDAB, an exothermic peak due to crystallization ($\Delta H = -28$ kJ mol$^{-1}$) is observed around 88 °C (heating rate: 10 °C min$^{-1}$), followed by an endothermic peak due to melting ($\Delta H = 47$ kJ mol$^{-1}$) at 183 °C. The DSC thermograms of p-MTDAB is shown in Fig. 1. The transparent, amorphous glassy states of m- and p-MTDAB are quite stable at room temperature, and no crystallization has been noticed over one year.

The formation of both the amorphous glassy state and the crystalline state for m- and p-MTDAB was also evidenced by X-ray diffraction. The X-ray diffraction patterns of the amorphous glassy samples of m- and p-MTDAB do not show any sharp peak characteristic of the crystal. On the other hand, when the amorphous glassy samples of m- and p-MTDAB are again heated above the crystallization temperature, characteristic sharp X-ray diffraction patterns are observed.

The present results indicate that the methyl substituent exerts a great influence on the formation of the glassy state. It is thought that incorporation of the methyl group into the non-planar starburst molecule TDAB increases the variety of conformations of the molecules and the mode of the packing of molecules, thus preventing crystallization.

p-MTDAB was found to exhibit unique solid-state morphology, polymorphism, in addition to the formation of the amorphous glassy state. That is, while m-MTDAB has only one crystalline form, p-MTDAB has three different crystalline forms. As shown in Fig. 1, when the crystalline sample of p-MTDAB obtained by recrystallization from benzene/hexane (crystal A) is heated, it melts at 198 °C, and then crystallization occurs instantly to form another crystal (crystal B), which melts at 210 °C to give an isotropic liquid (Fig. 1a). When the isotropic liquid is cooled down, the amorphous glassy state is spontaneously formed. When the amorphous glassy sample is again heated, a glass-transition phenomenon is observed at 58 °C, and then crystallization takes place around 88 °C to form another crystal (crystal C). Crystal C melts at 188 °C and crystallization takes place concurrently to form crystal B, which melts at 210 °C (Fig. 1b). These phenomena of crystallization from the melt were confirmed by a polarizing microscope. Among the three crystals which exist in p-MTDAB, crystal B has the lowest free energy. The difference between Fig. 1a and Fig. 1b in the temperature region higher than 180 °C may be ascribed to different rates of crystallization to form crystal B.

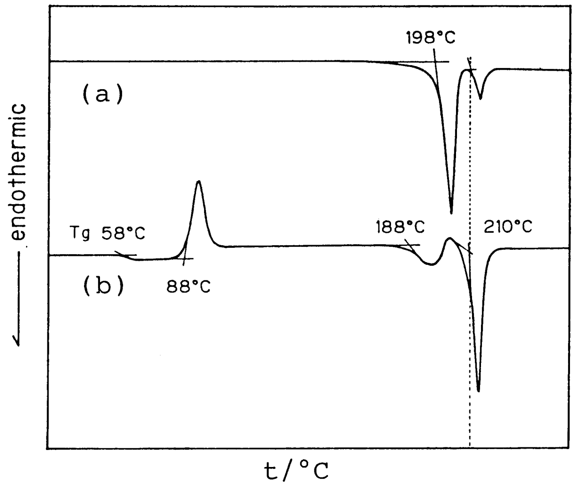


Fig. 1. DSC thermograms of p-MTDAB. Heating rate: 10 °C $\text{min}^{-1}$. The phase-transition temperatures were determined from the extraporated onset point. (a) Crystalline sample obtained by recrystallization (b) Amorphous glassy sample obtained by cooling the melt.

Figure 2 shows X-ray diffraction patterns of crystal A and crystal B together with the amorphous glass of p-MTDAB. The X-ray diffraction patterns of crystal A and crystal B are different from each other; however, crystal C exhibits essentially the same patterns with those of crystal A. It is suggested that the crystal structure of crystal C resembles that of crystal A.

The present study will enable molecular design of various starburst molecules based on TDAB for developing photo- and electro-active amorphous molecular materials. These materials including m- and p-MTDAB are expected to find potential application as functional materials, e.g., charge-carrier transport materials for photoreceptors and electroluminescence devices, materials for gas sensors, materials for photoelectrical conversion, and materials for memory devices.

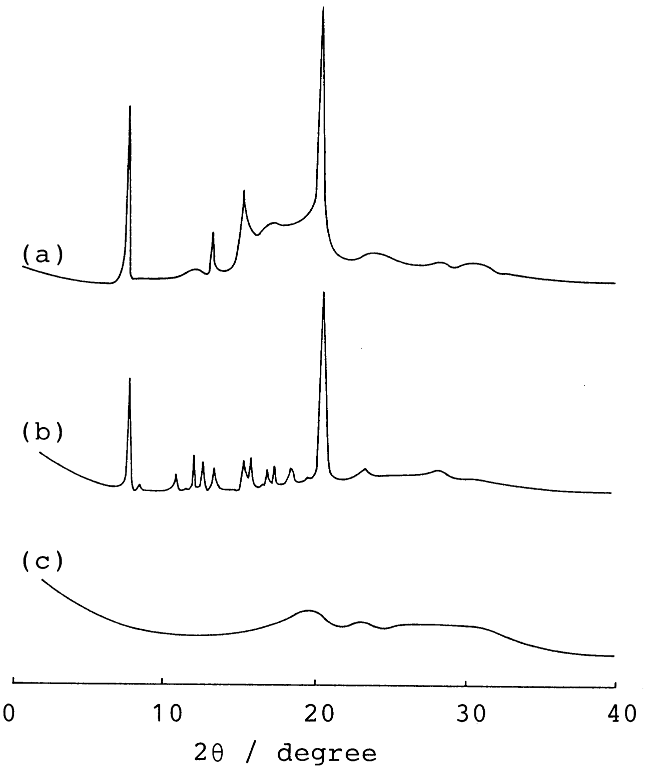


Fig. 2. X-Ray diffraction patterns of p-MTDAB. (a) Crystal A obtained by recrystallization (b) Crystal B obtained by heat treatment of the amorphous glass at ca. 205 °C for several minutes (c) Amorphous glass obtained by cooling the melt.

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