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Glass Formation and Phase Transition of Novel π-Electron Starburst Molecules, 1,3,5-Tris(phenyl-2-thienylamino)benzene and 1,3,5-Tris(phenyl-3-thienylamino)benzene

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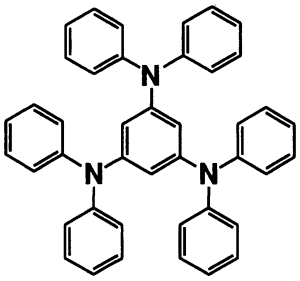
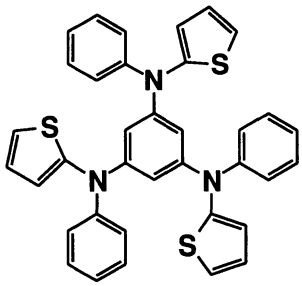
Novel π-electron starburst molecules, 1,3,5-tris(phenyl-2-thienylamino)benzene (α-TPTAB) and 1,3,5-tris(phenyl-3-thienylamino)benzene (β-TPTAB), are found to form amorphous glasses with well-defined glass-transition temperatures of 38 and 46 °C, respectively, while 1,3,5-tris(diphenylamino)benzene instantly crystallizes. The result leads to a concept of "increasing the number of conformers of nonplanar molecules" for a molecular design of amorphous molecular glasses. The glasses of α-TPTAB and β-TPTAB are found to be transformed finally into crystals with the highest melting points *via* metastable crystals on heating.

There are several organization states for molecular assemblies of organic compounds. They include single crystals, polycrystals, plastic crystals, liquid crystals, and amorphous glasses. With regard to organic amorphous glasses, polymers are well known. However, little attention has been paid to low-molecular-weight organic materials that form stable amorphous glasses above room temperature, although it is known that amorphous or quasi-amorphous films of certain organic compounds, *e.g.*, aromatic hydrocarbons, can be formed by vacuum deposition at low temperature.[1-4] Only a few examples of low-molecular-weight organic glasses with glass-transition temperatures higher than room temperature were known.[5,6] This is because low-molecular-weight organic compounds generally tend to crystallize readily. Developing such amorphous molecular materials is expected to open a new field in organic solid-state chemistry. We have recently found a few novel classes of π-electron systems for making amorphous glasses, which we refer to as π-electron starburst molecules in view of their molecular structures.[7-10] In order to establish guidelines for molecular design of amorphous molecular materials, an understanding of the correlation between molecular structure and glass-forming properties is required. Since the glassy state is a state of thermodynamic non-equilibrium, it tends to be transformed into a state of thermodynamic equilibrium. Such a relaxation phenomenon is also an important subject matter to be elucidated.

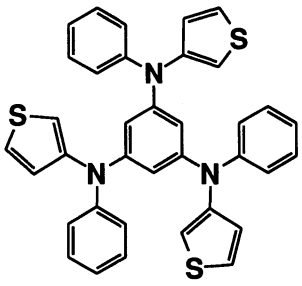
We report here that novel π-electron starburst molecules, 1,3,5-tris(phenyl-2-thienylamino)benzene (α-TPTAB) and 1,3,5-tris(phenyl-3-thienylamino)benzene (β-TPTAB), form readily amorphous glasses when the melt samples are rapidly cooled with liquid nitrogen, whereas 1,3,5-tris(diphenylamino)benzene (TDAB) instantly crystallizes, and that these glasses are transformed finally into crystals with the highest melting points *via* metastable crystals, respectively, on heating, exhibiting a marked difference in the mode of phase transformation. A guiding principle for molecular design of organic amorphous glasses is presented.



TDAB



α-TPTAB



β-TPTAB

Novel π-electron starburst molecules, α-TPTAB and β-TPTAB, were synthesized by the Ullmann reaction of 1,3,5-tris(phenylamino)benzene, which was obtained by the reaction of phloroglucinol with aniline, with 2-iodothiophene and 3-iodothiophene, respectively, in decalin at 170 °C for 14 h in the presence of potassium hydroxide and copper powder. Yield: 23 and 56% for α-TPTAB and β-TPTAB, respectively. They were purified by silica-gel column chromatography, followed by recrystallization from benzene/hexane or from cyclohexane, and identified by various spectroscopies, mass spectrometry and elemental analysis.[11)]

Both α-TPTAB and β-TPTAB were found to form easily transparent amorphous glasses when the melt samples were rapidly cooled with liquid nitrogen, whereas TDAB instantly crystallized. The formation of glasses was characterized by differential scanning calorimetry (DSC), X-ray diffraction, and polarizing microscopy. The result that the replacement of the three phenyl groups in TDAB by the thienyl group facilitates glass formation is thought to be due to the increase in the number of conformers for α-TPTAB and β-TPTAB relative to TDAB. X-Ray crystal structure analysis of a crystal of α-TPTAB obtained by recrystallization from cyclohexane shows that this molecule has a nonplanar molecular structure and that all the thienyl groups are disordered, each taking two positions which differ approximately by a 180° rotation along the single bond connecting the thiophene ring and the nitrogen atom.[12)] This result suggests that α-TPTAB can take several conformations with almost equivalent conformational energies and that the replacement of the three phenyl groups in TDAB by the thienyl groups increases the number of conformers of the molecule. It is thought that the increase in the number of conformers of nonplanar molecules prevents ready crystallization, facilitating the formation of a glass.

α-TPTAB and β-TPTAB were found to exhibit contrasting morphological changes. Figure 1 shows DSC curves of α-TPTAB. When a crystalline sample (crystal A) obtained by recrystallization from benzene/hexane or cyclohexane was heated, an endothermic peak due to a phase transition was observed at 169 °C, where the crystal A was transformed into a different crystal form (crystal B). Since neither an exothermic peak due to crystallization followed the endothermic peak in DSC curves nor the melting behavior was observed with a polarizing microscope, the phase transformation from the crystal A to the crystal B is regarded as a solid-solid transformation. On further heating, the crystal B melted at 187 °C to give an isotropic liquid (Fig. 1a). When the isotropic liquid was rapidly cooled down with liquid nitrogen, a transparent glass was formed. When the amorphous glass was again heated, a glass-transition phenomenon was observed at 38 °C, and then an exothermic peak due to crystallization to form another crystal (crystal C) was observed around 70 °C. Thereafter, an exothermic peak due to a solid-solid phase transition from the crystal C to the crystal B was observed around 133 °C, followed by the melting of the crystal B at 187 °C (Fig. 1b).

Figure 2 shows DSC curves of β-TPTAB. When a crystalline sample (crystal X) obtained by recrystallization from benzene/hexane or cyclohexane was heated, the crystal X was transformed into a different

crystal form (crystal Y) at 183 °C, followed by the melting of the crystal Y at 210 °C (Fig. 2a). The phase transformation from the crystal X to the crystal Y involves melting and crystallization. Although this mode of phase transformation was not clear in the DSC curve in Figure 2a, an exothermic peak due to crystallization following the endothermic peak at 183 °C was observed at a faster heating rate. In addition, the melting behavior of the crystal X followed by crystallization of the crystal Y was confirmed by polarizing microscopy. β-TPTAB was also found to form a transparent glass when an isotropic liquid was rapidly cooled with liquid nitrogen. When the amorphous glass was heated, glass transition took place at 46 °C, and then an exothermic peak due to crystallization to form another crystal form (crystal Z) was observed around 76 °C. On further heating, the crystal Z melted at 193 °C, followed by crystallization to form the crystal Y, which melted at 210 °C (Fig. 2b).

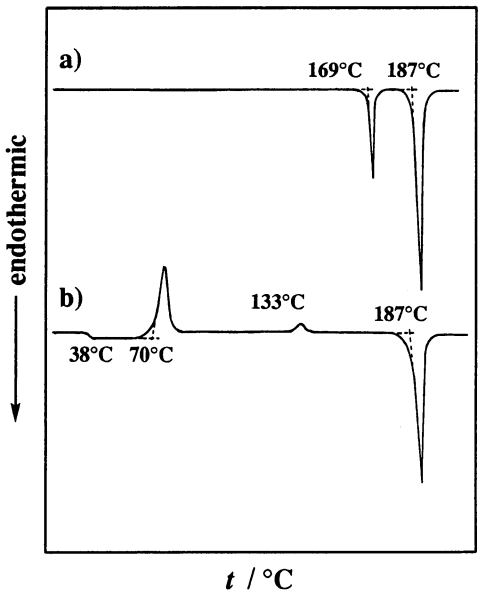


Fig. 1. DSC curves of α-TPTAB. (a) crystalline sample obtained by recrystallization from cyclohexane. (b) amorphous glass sample obtained by cooling the melt with liquid nitrogen. Heating rate: 5 °C min^{-1}.

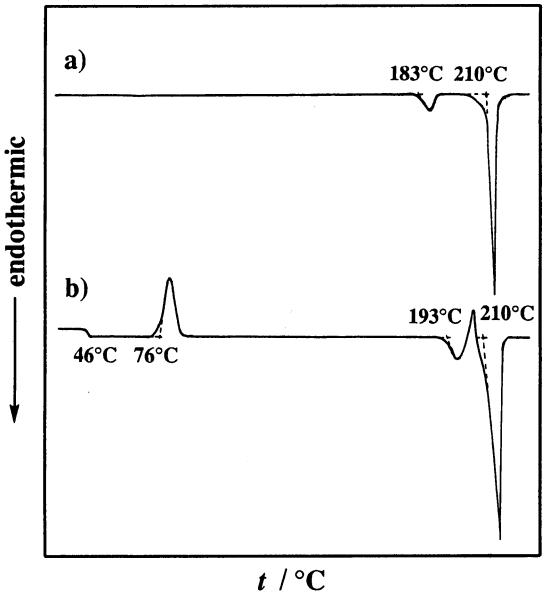
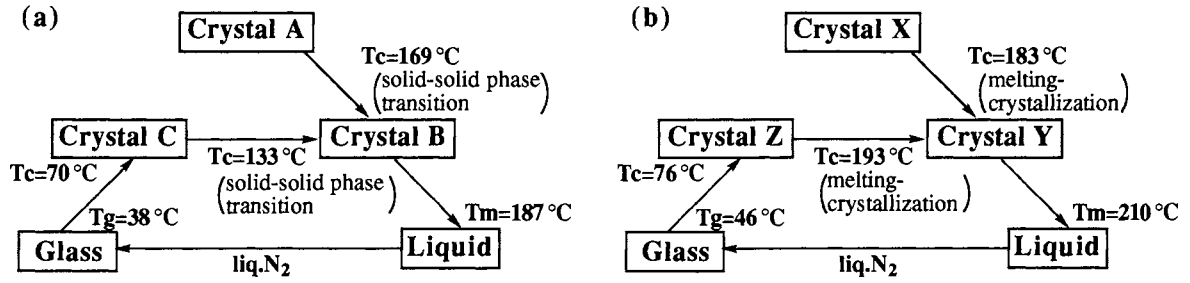


Fig. 2. DSC curves of β-TPTAB. (a) crystalline sample obtained by recrystallization from cyclohexane. (b) amorphous glass sample obtained by cooling the melt with liquid nitrogen. Heating rate: 5 °C min^{-1}.

The phase transformations observed for α-TPTAB and β-TPTAB are summarized in Scheme 1. It is of interest to note that the mode of phase transition changes drastically by a slight change of molecular structure. That is, while α-TPTAB undergoes solid-solid phase transitions from the crystal A to the crystal B and from the crystal C to the crystal B, β-TPTAB undergoes phase transitions involving melting and crystallization from the crystal X to the crystal Y and from the crystal Z to the crystal Y. The difference in the intermolecular packing in the molecular assemblies of α-TPTAB and β-TPTAB may be responsible for the difference in the mode of phase transition. The present results show that the relaxation from thermodynamically non-equilibrium glasses into the crystals with the highest melting points, crystals B and Y, takes place *via* liquids and the crystals C and Z in the metastable state.



Scheme 1. Morphological changes of (a) α-TPTAB and (b) β-TPTAB.

The present study presents an important concept for molecular design of amorphous molecular materials, *i.e.*, "increasing the number of conformers by lowering the symmetry of nonplanar molecules", which will enable the synthesis of a variety of novel π-electron starburst molecules based on TDAB for making amorphous molecular materials. The present study also reveals the relaxation process of the amorphous glass; the glasses of α-TPTAB and β-TPTAB are transformed finally into the crystals with the highest melting points *via* the metastable crystals, respectively.

References

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11) α-TPTAB: ^{1}H NMR (C_6D_6) δ=6.44-6.47 (dd, 3H), 6.49-6.51 (dd, 3H), 6.50-6.52 (dd, 3H), 6.71-6.76 (m, 3H), 6.87 (s, 3H), 6.92-6.98 (m, 6H), 7.12-7.15 (m, 6H) ppm. Found: C, 72.45; H, 4.59; N, 7.00; S, 16.07%. Calcd: C, 72.32; H, 4.56; N, 7.03; S, 16.09%. MS *m/e*=597 (M^+). β-TPTAB: ^{1}H NMR (C_6D_6) δ=6.46-6.47 (m, 3H), 6.66-6.68 (dd, 3H), 6.70-6.72 (dd, 3H), 6.74-6.77 (t, 3H), 6.75 (s, 3H), 6.96-6.99 (t, 6H), 7.08-7.10 (d, 6H) ppm. Found: C, 72.41; H, 4.46; N, 6.85; S, 16.02%. Calcd: C, 72.32; H, 4.56; N, 7.03; S, 16.09%. MS *m/e*=597 (M^+).
12) Crystal Data of α-TPTAB: $C_{36}H_{27}N_3S_3$, monoclinic, space group *C*2/c, a = 15.567(3), b = 12.957(4), c = 15.144(3) Å, β = 100.47(2)°, V = 3004(1) Å^3, Z = 4, Dc = 1.32 g cm^{-3}, μ(MoKα) = 2.78 cm^{-1}, R = 0.086, R_W = 0.048 for 1516 observed reflections. Dihedral angles between the plane of central benzene moiety and the plane consisting of the three carbon atoms bonded to the nitrogen atom are 45.7°, 45.7° and 51.5°. The population ratios of the three disordered thienyl groups are 0.73:0.27, 0.73:0.27 and 0.32:0.18. Details will be reported elsewhere.

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