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Hideyuki Nakano [a] , Emi Ueta [a] & Yasuhiko Shirota [a]

[a] Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

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Amorphous Molecular Material: Synthesis, Structure, and Glass-forming Properties of a Novel Starburst Molecule, 1,3,5-Tris(phenyl-3-thienylamino)benzene

HIDEYUKI NAKANO, EMI UETA, AND YASUHIKO SHIROTA*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

A novel π-electron starburst molecule, 1,3,5-tris(phenyl-3-thienylamino)-benzene (β-TPTAB), was designed and synthesized, and its morphological changes including glass formation were investigated in relation to the molecular structure. β-TPTAB was found to form readily an amorphous glass when the melt sample was rapidly cooled with liquid nitrogen. In addition, β-TPTAB was found to exhibit polymorphism, taking three different crystal forms depending upon the history of heat treatment. The X-ray crystal structure analysis of β-TPTAB shows that the molecule takes a nonplanar molecular structure and that the three thienyl groups are disordered: this is suggested to be responsible for the glass-forming properties of β-TPTAB.

Keywords: amorphous molecular material; glass; polymorphism; molecular structure; disorder

INTRODUCTION

Low molecular-weight organic compounds that readily form stable amorphous glasses above room temperature, which we refer to as amorphous molecular materials, are of interest as a novel class of organic materials. We have designed and synthesized several novel families of organic π-electron systems, which we refer to as "π-electron starburst molecules" in view of their molecular structures, for making amorphous molecular materials, and found that they readily form glasses with well-defined glass-transition temperatures (Tg).[1-9] They include 4,4',4"-tris(diphenylamino)triphenylamine (TDATA) and its derivatives,[1,2] derivatives of 1,3,5-tris(diphenylamino)benzene (TDAB),[3-5,7-9] and 1,3,5-tris[4-(diphenylamino)phenyl]benzene (TDAPB)

and its derivatives.[6]

With regard to the relationship between molecular structure and glass-forming properties, it should be noted that whereas TDAB readily crystallizes even when the melt sample is rapidly cooled with liquid nitrogen, methyl- or halogen-substituted derivatives of TDAB form amorphous glasses when the melt samples are cooled with liquid nitrogen or on standing in air.[3,4,8] It is suggested that the incorporation of substituents lowers the symmetry of the nonplanar molecule and hence increases the number of conformers of the molecule, facilitating glass formation.

In order to understand the relationship between molecular structure and glass-forming properties, we have designed and synthesized a new derivative of TDAB, 1,3,5-tris(phenyl-3-thienylamino)benzene (β-TPTAB), where three phenyl groups in TDAB are replaced by three thienyl groups, and investigated its glass-forming properties and morphological changes in relation to the molecular structure. A preliminary result has been reported as a communication.[10]

EXPERIMENTAL

Synthesis of β-TPTAB

1,3,5-Tris(phenylamino)benzene (1.757 g, 5 mmol) was reacted with 3-iodothiophene (7.089 g, 33.8 mmol) in decalin (10 ml) in the presence of potassium hydroxide (2.841 g, 50.6 mmol) and copper powder (2 g) at 170 °C for 14 h under nitrogen atmosphere. The crude product was extracted with hot benzene and chromatographed on silica-gel column by using a mixed solvent of benzene and hexane (1:1) as an eluent, followed by recrystallization from benzene/hexane or cyclohexane to give β-TPTAB as pale yellow needles (Crystal X in Fig. 1). Yield: 1.67 g (56 %). ^{1}H NMR (400 MHz, 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. UV (THF) λ_{max} (log ε) 295 nm (4.7). Anal. Calcd. for $C_{36}H_{27}N_3S_3$: C, 72.32; H, 4.56; N, 7.03; S, 16.09%. Found: C, 72.41; H, 4.46; N, 6.85; S, 16.02%. MS *m/e*=597 (M^+).

Apparatus

Differential scanning calorimetry (DSC) was carried out with a DSC220C (SEIKO I&E) calorimeter. X-Ray diffraction (XRD) was carried out with a Rotaflex RU200 (Rigaku) X-ray diffractometer. Polarizing microscopy was

carried out with a OPTIPHOT X2 (Nikon) microscope, fitted with a TH-600PM hot stage (Linkam) and crossed polarizers.

X-Ray Crystal Structure Analysis

A single crystal of β-TPTAB with a dimension of 0.18 x 0.29 x 0.30 mm^3 was grown by the recrystallization method from cyclohexane. The crystal data were as follows: $C_{36}H_{27}N_3S_3$, M=597.81, monoclinic, space group *C*2/c, a=15.498(2), b=12.997(2), c=15.250(2) Å, β=101.19(1)°, V=3013.4(5) $Å^3$, Z=4, Dc=1.26 gcm^{-1}, μ(Mo Kα)=2.51 cm^{-1}.

X-Ray diffraction data were collected by the ω-2θ scan technique up to 2θ=55° on Rigaku AFC-5R automatic four-circle diffractometer using graphite monochromatized Mo Kα radiation (λ=0.7107 Å). No significant intensity decay of three standard reflections was detected as measured after every 150 reflections. Of the 3752 reflections measured, 1175 reflections were observed ($|F_o| > 3\sigma(F_o)$). The intensity data were corrected for the Lorentz and polarization effects, but not for absorption.

The structures were solved by a direct method[11] and refined by a full-matrix least-squares method. Since the molecule has pseudo 2-fold symmetry, the site occupancy factors of a phenyl group (P2), which was refined as a rigid phenyl group, and a thienyl group (T2) were fixed to be 0.5. In addition, the refinement process revealed that the thienyl groups are disordered; each takes two positions which can almost overlap with each other by 180° rotation about the bond connecting the thienyl group and the nitrogen atom. Therefore, all the atoms of the thienyl group were assumed to be completely overlapped with those of the disordered thienyl group and the site occupancy factors of sulfur atoms were refined. Non-hydrogen atoms were refined anisotropically except the atoms on the phenyl group P2 and the thienyl group T2, which were refined isotropically.

The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where weighting function was $w=1/\sigma^2(F_o)$. The atomic scattering factors were taken from those of the International Tables for X-Ray Crystallography.[12] R and Rw values at the last stage were 0.078 and 0.062, respectively.

RESULTS AND DISCUSSION

Glass Formation and Polymorphism of β-TPTAB

The novel starburst molecule β-TPTAB, which was obtained as a crystal by

recrystallization from a cyclohexane solution, was found to form readily an amorphous glass when the melt sample was rapidly cooled with liquid nitrogen. This contrasts the behavior of TDAB, which readily crystallizes even when the melt sample is rapidly cooled with liquid nitrogen. In addition, β-TPTAB was found to exhibit polymorphism, taking three different crystal forms depending upon the history of heat treatment.

Fig. 1 shows DSC curves of β-TPTAB. When the crystal sample (Crystal X) obtained by recrystallization from cyclohexane was heated, an endothermic peak due to solid-solid phase transformation to give a different crystal form (Crystal Y) was observed at 183 °C, followed by melting of the Crystal Y at 210 °C. When the isotropic liquid was cooled rapidly with liquid nitrogen, an amorphous glass was obtained. When the glass sample was again heated, a glass-transition phenomenon was observed 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. The formation of the amorphous glass and three kinds of crystals was also

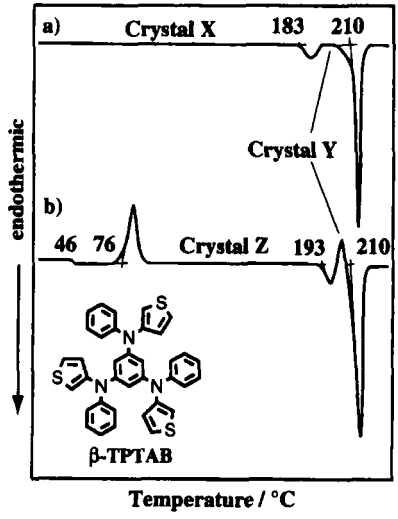

FIGURE 1 DSC curves of β-TPTAB. a) Crystal sample obtained by recrystallization (Crystal X) was heated. b) Glass sample obtained by cooling the melt was heated.

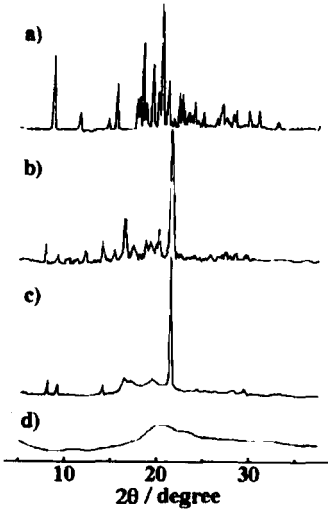

FIGURE 2 XRD patterns of β-TPTAB. a) Crystal X, b) Crystal Y, c) Crystal Z, d) glass

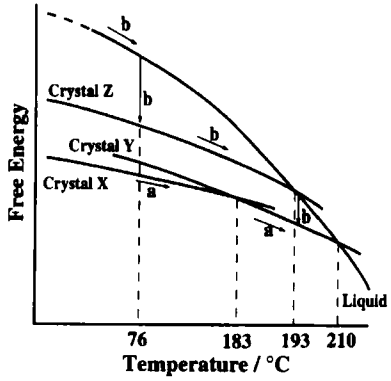

FIGURE 3 Schematic free energy - temperature curves for β-TPTAB.

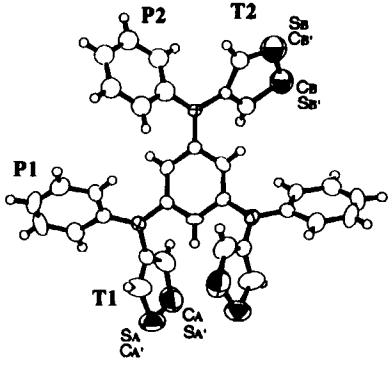

FIGURE 4 Molecular structure of β-TPTAB.

confirmed by XRD (Fig. 2) and polarizing microscopy. Whereas the sample obtained by cooling the melt with liquid nitrogen showed only a broad halo in the XRD pattern, the Crystals X, Y, Z showed sharp peaks characteristic of crystals, which were different from one another.

The schematic free energy - temperature curves for the morphological changes of β-TPTAB are shown in Fig. 3, where morphological changes from the Crystal X and from the glass are indicated by the arrows a and b, respectively.

Molecular Structure of β-TPTAB

In order to obtain information on the relationship between molecular structure and glass-forming properties, the X-ray crystal structure analysis of β-TPTAB was carried out for the Crystal X. Fig. 4 shows the molecular structure of β-TPTAB. β-TPTAB has a nonplanar molecular structure, where the dihedral angles between the least square plane of the central benzene ring and those of the thienyl groups (T1 and T2) and the phenyl groups (P1 and P2) are 89°, 72°, 60°, and 62°, respectively. In addition, all the thienyl groups in β-TPTAB are disordered; each thienyl group takes two positions which can almost overlap with each other by 180° rotation about the bond connecting the thienyl group and the nitrogen atom. The population ratios of the disordered thienyl groups T1 and T2 are 0.56:0.44, and 0.33:0.17, respectively, as estimated from the values of the site occupancy factors (sof) of sulfur atoms (sof(SA):sof(SA') and sof(SB):sof(SB')).

Relationship between Molecular Structure and Glass-Forming Properties

In contrast to TDAB, which readily crystallizes instead of forming a glass, the novel starburst molecule, β-TPTAB, was found to form readily an amorphous glass with a Tg of 46 °C when the melt sample was cooled with liquid nitrogen. In addition, β-TPTAB is of interest in that it exhibits polymorphism involving solid-solid phase transformation and crystallization from the supercooled liquid and the melt. As in the case of the asymmetrical substitution at the phenyl group in TDAB,[3,4,8] the replacement of three phenyl groups in TDAB by three thienyl groups is suggested to lower the symmetry of the nonplanar molecular structure and to increase the number of conformers with almost equivalent conformational energies, facilitating the formation of the glass. The phenomenon of polymorphism observed for β-TPTAB and its disordered molecular structure are in support of this idea. The present study presents an important concept , "lowering the symmetry of a nonplanar molecule", for the molecular design for amorphous molecular materials.

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