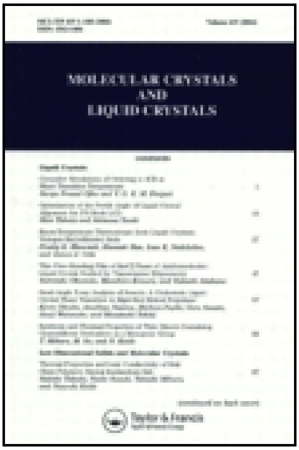

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Amorphous Molecular Materials: Synthesis and Properties of a Novel Starburst Molecule, 4,4′,4″-Tri(N-Phenoxazinyl)Triphenylamine

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AMORPHOUS MOLECULAR MATERIALS : SYNTHESIS AND PROPERTIES OF A NOVEL STARBURST MOLECULE, 4,4',4"-TRI(*N*-PHENOXAZINYL)TRIPHENYLAMINE

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Abstract A novel starburst molecule, 4,4',4"-tri(*N*-phenoxazinyl)triphenylamine (TPOTA), has been synthesized, and its molecular properties and morphology investigated. TPOTA readily forms a stable amorphous glass with a glass transition temperature as high as 145°C when the melt sample is cooled down on standing, as characterized by differential scanning calorimetry and X-ray diffraction.

INTRODUCTION

Amorphous materials, *e.g.*, amorphous inorganic materials and amorphous metals, have recently received attention as novel functional materials with excellent processabilty, flexibility, isotropic properties, homogeneous properties owing to the absence of grain-boundaries, etc. As for amorphous organic materials, polymers and composite polymer systems, where low-molecular-weight functional organic materials are dispersed in polymer binders, have also received attention both from fundamental and from practical viewpoints. However, little attention has been paid to low-molecular-weight organic materials that form stable amorphous glasses above room temperature,[1,2] since low-molecular-weight organic compounds generally tend to crystallize readily. Low-molecular-weight organic compounds that form stable glasses above room temperature are expected to constitute a novel class of functional organic materials which show a glass transition usually associated with amorphous organic polymers.

For the purpose of developing photo- and electro-active amorphous molecular materials, we have been studying the synthesis and properties of novel starburst molecules consisting of π-electron systems. We have reported a novel class of π-conjugated starburst molecules, 4,4',4"-tris(diphenylamino)triphenylamine (TDATA) and its methyl-substituted derivative, 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA).[3] They have been found to form readily stable amorphous glasses with glass transition temperatures of 89 and 75°C, respectively, when the melt samples are cooled.

In applying amorphous molecular materials for electronic devices such as electroluminescent devices, it is desirable that the glass transition temperature (Tg) should be as high as possible. For the morphological change of amorphous materials, which is often caused by Joule heat, leads to the deterioration of the devices.

With the aim of developing amorphous molecular materials having higher Tg, we have synthesized a novel starburst molecule incorporating a rigid moiety of phenothiazine, 4,4',4"-tri(*N*-phenothiazinyl)triphenylamine (TPTTA),[4] and found that the material has a much higher Tg than TDATA and *m*-MTDATA.

We report here the synthesis, molecular properties and morphology of a novel starburst molecule containing a structurally rigid moiety of phenoxazine, 4,4',4"-tri(*N*-phenoxazinyl)triphenylamine (TPOTA).

EXPERIMENTAL

Materials

Phenoxazine was prepared according to the method in the literature.[5] 4,4',4"-Tri(*N*-phenoxazinyl)triphenylamine (TPOTA) was synthesized by the reaction of phenoxazine (2.64 g, 14.4 mmol) with 4,4',4"-triiodotriphenylamine[1] (2.0 g, 3.2 mmol) in the presence of copper powder (2.0 g) and potassium hydroxide (1.69 g, 28.8 mmol) at 180°C in decalin (4 ml) for 6 hr under nitrogen. TPOTA was isolated by silica gel column chromatography (crude yield: 50 %) and purified by recrystallization from benzene to give colorless prisms. Crystalline samples obtained by recrystallization from benzene contained the solvent; therefore, they were heated to 100°C in vacuum to remove the solvent molecules. TPOTA was identified by IR, UV and ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis.

MS: m/e 788(M$^+$). Found: C, 82.33; H, 4.51; N, 7.14%. Calcd. for $C_{54}H_{36}N_4O_3$: C, 82.21; H, 4.60; N, 7.10; O, 6.08%. UV(λ_{max}, log ε): 311 nm, 4.7. ^{1}H NMR (C_6D_6): δ 6.13 (6H, m), 6.53 (12H, m), 6.80 (6H, m), 6.87 (6H, m), 7.08 (6H, m).

Measurements

Emission spectra were measured for a dilute solution of TPOTA in tetrahydrofuran (THF). The phosphorescence spectra were measured for a solution prepared in a quartz tube (ϕ 5 mm) degassed by repeated freeze-pump-thaw cycles. The fluorescence quantum yield was determined at room temperature relative to that of quinine bisulfate in an aqueous sulfuric acid (0.5 mol dm^{-3}, $\Phi_f = 0.55$).

Cyclic voltammetry was performed using the three electrode system. A Pt disk

(0.20 cm^2), a Pt wire, and a Ag/AgNO$_3$ (0.01 mol dm^{-3} in acetonitrile) were used as the working, counter, and reference electrodes, respectively. The dichloromethane solution of TPOTA (1 x 10^{-3} mol dm^{-3}) containing tetrabutylammonium perchlorate (0.1 mol dm^{-3}) as a supporting electrolyte was deoxygenated by passing nitrogen.

Morphological changes were characterized by differential scanning calorimetry (DSC) and X-ray diffraction.

Apparatus

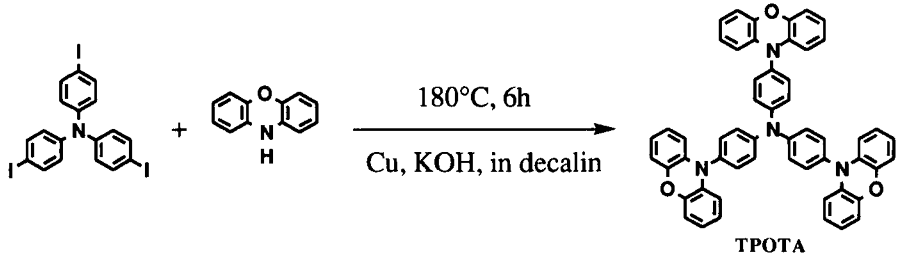
Electronic absorption spectra were recorded with a Hitachi U-3200 spectrophotometer. Emission spectra were measured with a Hitachi 850 fluorescent spectrophotometer. The fluorescence lifetime was measured with a Horiba NAES-1100 time resolved spectrofluorometer.

Cyclic voltammetry was carried out with a Hokuto Denko HA-501 potentiostat/galvanostat, a Hokuto Denko HB-104 function generator, and a Rikadenki RW-21 X-Y recorder. DSC measurements were made with a Seiko DSC220C.

RESULTS AND DISCUSSION

Synthesis of 4,4',4"-tri(*N*-phenoxazinyl)triphenylamine (TPOTA)

With the aim of developing thermally stable amorphous molecular materials, a novel starburst molecule having a structurally rigid moiety of phenoxazine, TPOTA, was synthesized by the Ullmann reaction of 4,4',4"-triiodotriphenylamine with phenoxazine in a yield of *ca.* 50 % , as shown in Scheme 1. TPOTA was obtained as colorless crystals.



SCHEME 1 Synthesis of TPOTA

Molecular properties

Figure 1 shows the electronic absorption and emission spectra of TPOTA in THF. The electronic absorption spectrum of TPOTA (λ_{max}=311 nm, log ε=4.6) appears to be a superposition of those of phenoxazine (λ_{max}=318 nm, log ε=3.9) and triphenylamine (λ_{max}=299, log ε=4.5). The result implies that the TPOTA molecule is not well wholly π-conjugated. On the other hand, the fluorescence spectrum of TPOTA in THF at room temperature shows a significant red-shift relative to those of triphenylamine and phenoxazine.[6] These results imply that the TPOTA molecule in the electronically excited singlet state is more significantly π-conjugated than that in the ground state, probably due to the change in the molecular structure, *i.e.*, increase in the degree of the planarity of the molecule. The fluorescence quantum yield in THF and fluorescence lifetime in 2-methyltetrahydrofuran (MTHF) at room temperature for TPOTA were 0.015 and 1.8 ns, respectively. The phosphorescence spectrum of TPOTA in MTHF at 77K was observed in the wavelength region from 445 nm to 600 nm (λ_{max}=457, 470, and 492 nm with shoulders at 510 and 520 nm). The phosphorescence lifetime at 77 K was 2.0 s. The phosphorescence was much more intense than the fluorescence, and the ratio of the quantum yield of phosphorescence to that of fluorescence (Φ_p/Φ_f) was 5.9.

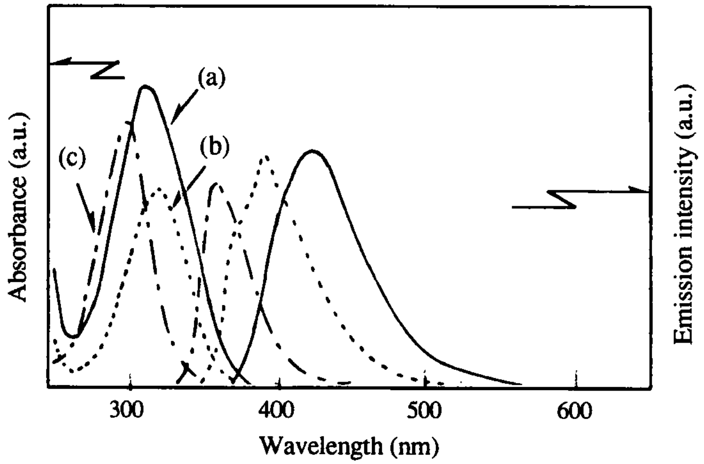


FIGURE 1 Electronic absorption and fluorescence spectra in THF at room temperature. (a) TPOTA, (b) phenoxazine, (c) triphenylamine

Figure 2 shows cyclic voltammograms for the anodic oxidation of TPOTA measured at a scan rate of 100 mV s^{-1}. The value of i_{pc}/i_{pa} was nearly 1.0, but the peak potential slightly depended upon the scan rate. Thus, the anodic oxidation process is chemically reversible, but electrochemically quasi-reversible in the range of the present experiment. The half-wave oxidation potential ($E_{1/2}^{ox}$) of TPOTA was 0.46 V vs. Ag/Ag$^+$(0.01 mol dm^{-1}). This value is lower than that for triphenylamine ($E_{p/2}^{ox}$ =

0.73 V), but higher than that for phenoxazine ($E_{1/2}^{ox}$ = 0.34 V). These results show that the phenoxazine moiety and the triphenylamine moiety in TPOTA are not wholly π-conjugated.

The electronic absorption spectrum of the anodically oxidized TPOTA shows a band with λ_{max} at 540 nm. It is known that the phenoxazine radical cation produced chemically has an intense absorption maximum at 530-535 nm.[7] Thus, the absorption band of the TPOTA radical cation resembles that of the phenoxazine radical cation.

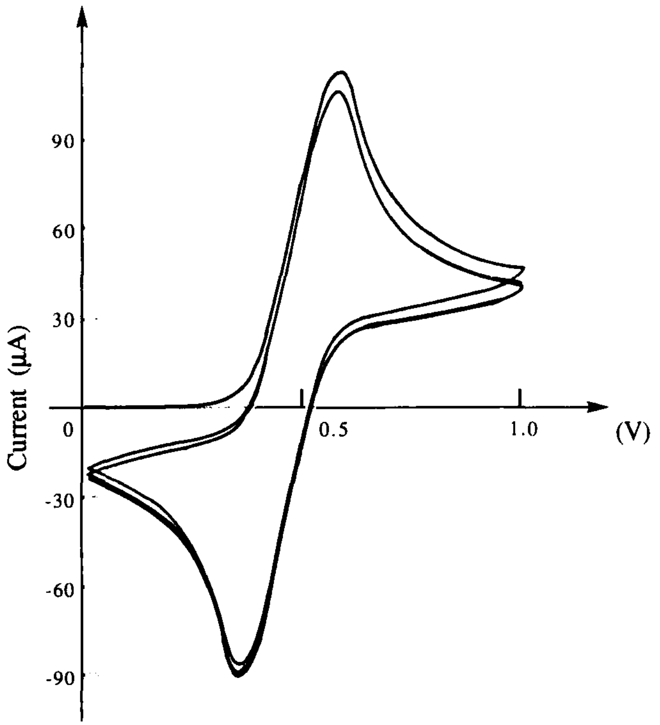


FIGURE 2 Cyclic voltammograms for the anodic oxidation of TPOTA in CH_2Cl_2. Scan rate: 100 mV s^{-1}

Morphology

Figure 3 shows DSC curves of TPOTA. When the crystalline sample of TPOTA obtained by recrystallization from benzene was heated, an endothermic peak due to the evaporation of benzene retained in the TPOTA crystals was observed at around 90°C, followed by another endothermic peak due to the melting at 341°C. When the melt sample is cooled down, it readily forms a transparent, stable amorphous glass *via* a supercooled liquid state, being independent of the cooling rate in the time scale of the experiments. When the glassy sample was heated, a glass transition phenomenon was observed at 145°C, and on further heating above Tg, crystallization took place at around 176°C, followed by dual meltings (Tm' = 329, Tm = 341°C). The origin of the dual meltings is not clear at present. The specific heat change at Tg was 200 J $\text{deg}^{-1}\text{mol}^{-1}$, and the enthalpy changes for the crystallization and for the melting were -31.6 and 46.9 kJ mol^{-1}, respectively.

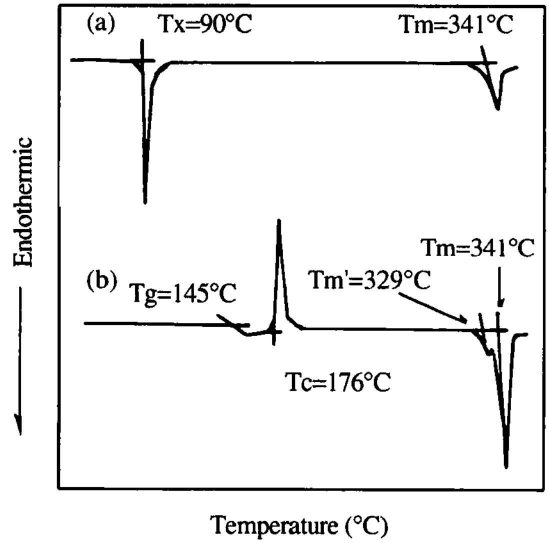


FIGURE 3 DSC curves of TPOTA. Heating rate : 5°C min^{-1}.
(a) Crystalline sample obtained by recrystalization from benzene.
(b) Glassy sample obtained by cooling the melt.

The formation of the amorphous glassy state and the crystalline state was evidenced by X-ray diffraction (Figure 4). Whereas the glass of TPOTA shows only broad halos, the crystalline sample obtained by heating the amorphous glass over Tg exhibits sharp peaks characteristic of the crystal. The transparent, amorphous glassy state of TPOTA is stable at room temperature. No crystallization has been noticed over two years.

A nonplanar molecular structure of TPOTA is thought to be responsible for its ready glass formation. The high Tg of TPOTA is attributed to the incorporation of the rigid moiety of phenoxazine, since Tg for amorphous molecular materials is thought to be the temperature at which molecular motions corresponding to micro Brownian motions for polymers, which are caused by intramolecular bond rotations, start to take place. The Tgs of TPOTA and TPTTA do not differ significantly (Tg: 145°C for TPOTA, 141°C for

TPTTA); however, TPOTA has a much higher melting point than TPTTA (Tm: 341°C for TPOTA, 288°C for TPTTA). Stronger intermolecular interactions for TPOTA than for TPTTA may be due to different crystal structures, *i.e.*, different packing of the molecules between TPOTA and TPTTA, as revealed from X-ray diffraction patterns.

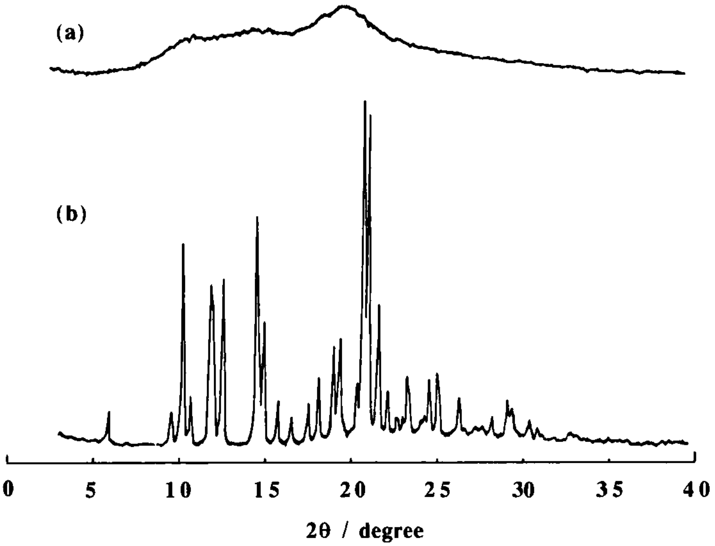


FIGURE 4 X-ray diffraction patterns of TPOTA
(a) Glassy sample obtained by cooling the melt
(b) Crystalline sample obtained by heating the glass

SUMMARY

We have synthesized a novel starburst molecule for amorphous molecular materials, 4,4',4"-tri(*N*-phenoxazinyl)triphenylamine (TPOTA), and found that this compound readily forms a stable glass with a high glass transition temperature of 145°C.

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