Preparation of new branched poly(triphenylamine)

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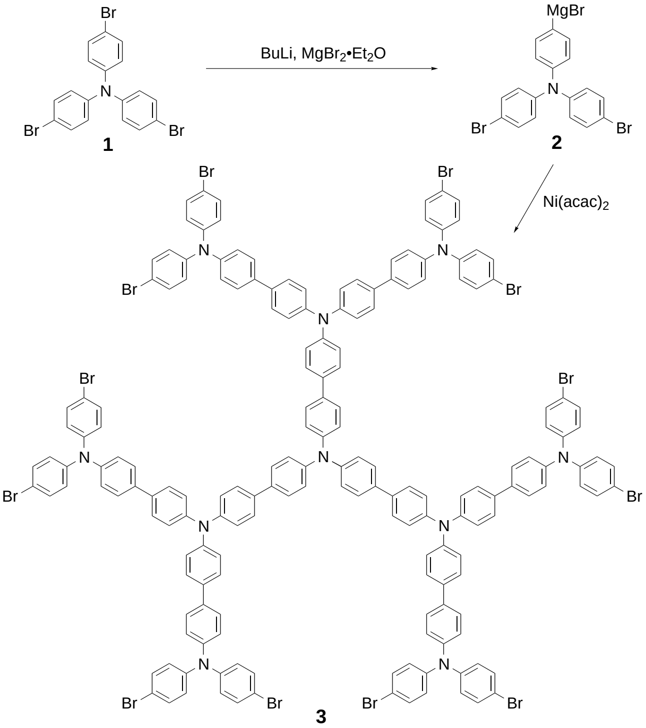
New branched poly(triphenylamine) is conveniently prepared by the Grignard reaction of tris(4-bromophenyl)-amine.

Oligomeric and polymeric materials based on triphenylamine have attracted much attention because of their stability and useful properties such as electrical conductivity and electroluminescence.[1–3] Typical conductive polymers have a linear conjugated system like polythiophene, polyphenylene and polypyrrole. Until now, only a few reports have appeared on three dimensionally conjugated polymers.[4–6]

We report here the first preparation of a branched conjugated polymer containing triphenylamine, *via* the coupling of *N*,*N*-bis(4-bromophenyl)-*N*-(4-bromomagnesiophenyl)amine **2**, by the Grignard reaction of tris(4-bromophenyl)amine **1** (Scheme 1).

Branched polymers can be prepared through two distinct synthetic approaches. One is a stepwise growth process,[7,8] in which a protection–deprotection step is required at every stage. Although this approach yields monodisperse polymers with well-defined structure, it usually requires extensive purification of the products at every protection–deprotection step of the growth process. Another approach is the one-step process[9,10] where an AB_x-type monomer undergoes self-condensation polymerization, as first discussed theoretically by Flory in 1952,[11] which results in a branched product. The advantage of this one-pot AB_x approach lies in its simple preparation process. But this method involves the loss of control in molecular weight, accompanied by a broad molecular weight distribution.



Scheme 1

Polymer **3** was prepared by monolithiation with Bu^{n}Li at −78 °C in THF, followed by reaction with magnesium bromide–diethyl ether, and coupling the resulting Grignard reagent with the catalytic amount of Ni(acac)$_2$. Grignard reagent **2** reacted as an AB_2-type monomer to give branched conjugated polymer **3** in a one-step process. Polymer **3** had an average molecular weight of 4.0×10^3 and was found to be soluble in organic solvents such as THF and $CHCl_3$, which implies that the branched polymer is processable.

A FTIR spectrum of monomer **1** showed three bands at 510, 817 and 1269 cm^{-1}, assignable to the C–Br stretching vibration; the C–H deformation vibration of 1,4-disubstituted benzene rings and the C–N stretching vibration of tertiary amines, respectively. Polymer **3** had all these bands, but the band at 510 cm^{-1} was weak, due to the C–Br stretching vibration of the terminal benzene rings. These results indicate that a C–C bond was formed between the monomers at the carbon atoms coupled with bromine originally and a highly conjugated system was formed.

The UV–VIS spectra of monomer **1** had a band at 307 nm assignable to the conjugation between benzene units and nitrogen atoms. In polymer **3** a new π–π^* transition band was clearly observed at 360 nm, possibly brought about by the conjugation between biphenylene units and nitrogen atoms.

The ^{13}C NMR spectrum of polymer **3** had three bands at 124.4, 127.5 and 129.3 ppm, which were assignable to biphenylene carbon resonances. Monomer **1** did not have these bands.

GPC was performed in THF at 40 °C using a TOSOH TSKgel G3000H$_{XL}$ column which was calibrated with polystyrene standards. Fig. 1 shows a fully reproducible GPC trace. The molecular weight of the lowest oligomeric peak was *ca*. 1000, indicating that the lower oligomers had been removed in the course of the work-up. The GPC trace had another interesting feature; the splittings of the low oligomeric peaks reflect the resolution of the repeating unit of polymer **3**, $C_{18}H_{12}NBr$. The results of GPC indicated that the degree of polymerization was *ca*. 12. Considering that the repeating unit of polymer **3** contains three benzene rings, this degree of polymerization signifies that the polymer contained *ca*. 36 benzene rings, which was sufficient to show electroactivity as described below. The degree of polymerization estimated from the bromine content of polymer **3** was *ca*. 10, which implies that the value obtained by GPC was likely to be an overestimate of the real molecular weight.

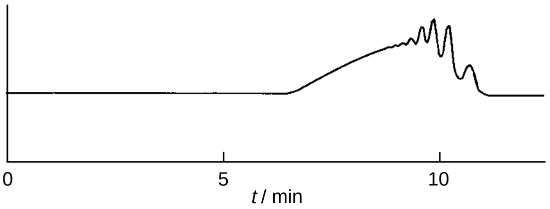


Fig. 1 GPC of polymer **3** in THF

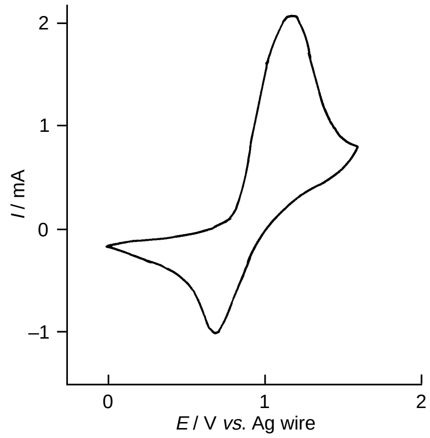


Fig. 2 Cyclic voltammogram of polymer **3** in PC with 0.1 mol l^{-1} Bu$_4$NBF$_4$; sweep rate, 100 mV s^{-1}

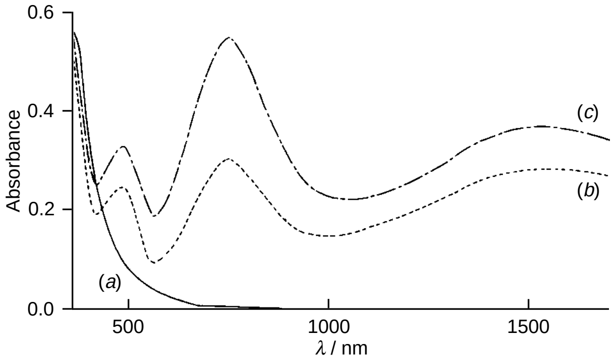


Fig. 3 Spectral change during electrochemical BF$_4^-$ doping of polymer **3**. Applied voltage: (*a*) 0 , (*b*) 1.0 and (*c*) 1.2 V.

A cast film deposited on a platinum plate was used for cyclic voltammetry. The polymer showed a cathode-activity at applied voltages higher than 0 V; an anodic peak was observed at 1.20 V (Fig. 2). The film was dark blue above the oxidation potential and brown–yellow in the neutral state. The amount of charge, *Q*, exchanged during the redox cycle, was calculated from the integration of the absolute value of the current in Fig. 2 with respect to sweep time. The value of *Q* was found to be 0.20 electron per monomeric unit, which indicated that the polymer would be useful as a charge storage material.

Fig. 3 shows the change in the VIS–near IR spectra during electrochemical doping of polymer **3**. When the applied voltage was 0 V, the polymer film had only one band at 360 nm (3.44 eV) assigned to a π–π* transition. At 1.0 and 1.2 V, three new bands were observed around 500, 750 and 1500 nm (2.48, 1.65 and 0.83 eV). The first and last bands were considered to be assigned to the transition from the valence band to the higher and lower polaron bands,[12] respectively. The second band would be due to the transition from the lower to the higher polaron band. Electrochemically created charge carriers would be identified as polaron species in this case. The stability of the charge carriers would be brought about by the resonance effect of charged triphenylamine moiety.

Many conductive polymers are insoluble in organic solvents due to the rigid main chains but the introduction of a long alkyl or alkoxy group to the main chains is one way of enhancing solubility. However these groups do not contribute to an increase in π-conjugation length. A new branched conjugated polymer containing triphenylamine has been designed which has both a hyperbranched and conjugated backbone, and was found to be soluble in organic solvents without the addition of a long alkyl or alkoxy group. It showed a distinct anode-activity, indicating that it has a highly developed conjugated system.

Footnote and References

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