

Preparation of hyperbranched copolymers containing triphenylamine and divinylbenzene units

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Abstract

In the presence of palladium(II) acetate, the coupling reaction of tris(4-bromophenyl)amine **1** and *p*-divinylbenzene **2** gave a hyperbranched conjugated copolymer **4** in a one step process and in a high yield. Polymer **4** was soluble in organic solvents such as THF and chloroform. GPC indicated that it had an average molecular weight of 5.1×10^3 . A cast film had an anodic peak at 1.05 V vs Ag wire. It was blue above the oxidation potential and light-yellow in the neutral state.

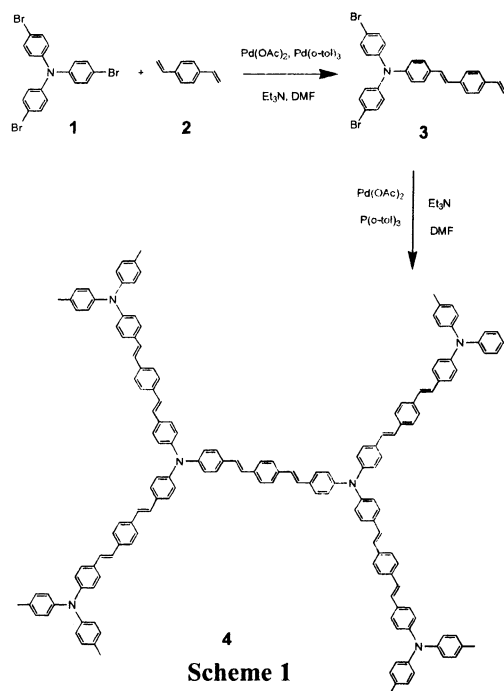
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1. Introduction

Dendritic macromolecules and hyperbranched polymers have received considerable attention because of their unique chemical and physical properties [1-4]. There are two types of dendrimers reported as organic light-emitting materials. One is dendrimers with fully-conjugated skeletons [5]; the other is electroactive chromophores connected by insulating dendrons [6]. A large number of papers have been published on electroluminescent (EL) dendrimers. On the other hand, hyperbranched polymers as light-emitting materials are limited [7].

Triphenylamines (TPAs) have been used most widely as the hole-transporting layer in EL devices, due to their amorphous film-forming ability and their high carrier mobility [8].

In this study, we report the preparation of new conjugated alternate copolymers constituted of triphenylamine and divinylbenzene units by the palladium catalyzed coupling of tris(4-bromophenyl)amine **1** and *p*-divinylbenzene **2** (Scheme 1).



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Amine **1** and divinylbenzene **2** are trifunctional(B_3) and difunctional(A_2) monomers, respectively. Hyperbranched polymers can be prepared through intermediate AB_2 monomers **3** formed from B_3 and A_2 monomers [9]. The copolymer was soluble in organic solvents such as chloroform and THF. GPC indicated that it had an average molecular weight of 5.1×10^3 . The cyclic voltammogram of the polymer film showed reversible p-type doping and undoping with a color change between light-yellow (undoped) and blue (doped).

2. Experimental

2.1. Characterization

FTIR measurements were performed on a Perkin-Elmer 1720-X spectrometer. UV-VIS spectra were recorded on a Shimadzu UV-3100PC spectrometer. GPC was performed in THF at 40 °C using a TOSOH TSKgel G3000Hxl column which was calibrated with polystyrene standards. Cyclic voltammograms were measured in a 0.1 mol/l Bu_4NBF_4 solution of propylene carbonate at a sweep rate of 100 mV/s by using an ALS 660 electrochemical analyzer. A platinum plate and a Ag wire were used as counter and reference electrodes, respectively. Working electrode was a platinum plate or indium-tin oxide glass (ITO).

2.2. Polymerization

A typical experimental procedure is as follows. The mixture of tris(4-bromophenyl)amine (578 mg, 1.2 mmol), *p*-divinylbenzene (155 mg, 1.2 mmol), palladium (II) acetate (11 mg, 0.05 mmol) and tri(*o*-tolyl)phosphine (71 mg, 0.23 mmol) were stirred in anhydrous DMF (100 ml) and triethylamine (2 ml) overnight at 100 °C under argon. The reaction mixture was poured into 60 ml of 1 N HCl to afford light yellow powder almost quantitatively. The resulting polymer was soluble in organic solvents and contained large amount of bromines, which is similar to the case for conventional hyperbranched polymers prepared from AB_2 type monomers [10].

3. Results and Discussion

3.1. Polymer synthesis

Polycondensation of amine **1** and divinylbenzene **2** with the feed ratio of 1/1 was carried out in anhydrous DMF. Reaction conditions and results are summarized in Table 1. When the concentration of **1** or **2** was as high as 0.06 mol/l or lower, the resulting polymer was soluble in organic solvents such as chloroform and THF (Exp. Nos. 1-3). On

the other hand, above this concentration, gelation occurred within 1-2 h during the polymerization (Exp. Nos. 4-5). In the following study, polymerization was conducted under the conditions of Exp. No. 1 in Table 1.

Table 1. Reaction conditions of polymerization and polymer solubility

Exp. No.	1 (mmol)	2 (mmol)	DMF (ml)	Concn ^a (mol/l)	Polymer solubility
1	1.2	1.2	100	0.012	⊙
2	1.2	1.2	40	0.03	○
3	1.2	1.2	20	0.06	○
4	1.9	1.9	10	0.19	Gel
5	1.9	1.9	5	0.38	Gel

a: the concentration of **1** or **2**

3.2. Molecular Weight

Fig. 1. shows a fully reproducible GPC trace of polymer **4**. The molecular weight of the lowest oligomeric peak was about 500, suggesting that the polymer **4** was prepared through intermediate AB_2 monomers **3** formed from B_3 and A_2 monomers. The GPC trace had another interesting feature: the splitting of the low oligomeric peaks reflect the resolution of the repeating unit of polymer **4**, $C_{28}H_{20}N$. The results of GPC indicated that the degree of polymerization was about 14. Considering that the repeating unit of polymer **4** contains four benzene rings, this degree of polymerization signifies that the polymer contained about 56 benzene rings, which was sufficient to show electroactivity as described below.

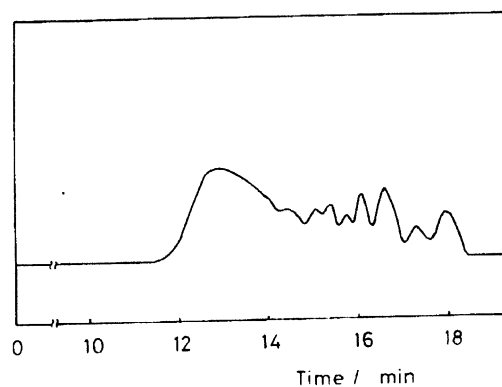


Fig. 1. GPC of polymer **4** in THF.

3.3. FTIR, UV-VIS and luminescence spectra

Fig. 2 shows FTIR spectra of amine **1** and polymer **4**. Amine **1** has three bands at 510, 817 and 1269 cm^{-1} ,

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