Electrical and magnetic properties of electro-oxidative polymerized poly(tris(thienylphenyl)amine)s

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Abstract

Electro-oxidative polymerized poly(tris(thienylphenyl)amine)s, which have the hyperbranched (dendritic) structure (PTPA) and linear type (PMeTPA), were investigated for their electrical and magnetic properties. The conductivity PTPA showed was almost one order higher than that of PMeTPA. From the solid state ESR measurements of the polymers, observation of ESR signal at $g \approx 2.0027$ and 2.0030 indicated the formation of a triphenylamine cation radical. The normalized magnetization plots ($M/M_s$) for PTPA and PMeTPA are close to the theoretical Brillouin curves for $S=1$, indicating a magnetic interaction between the spin centers in PMeTPA. The spin concentrations determined by the $M_s$ values of PTPA and PMeTPA were 7.3–7.4 and 1.3–1.4%, respectively. This large difference in the spin concentration of the polymers according to the structure resulted from a different spin conformation by the radical structure.

Keywords: Poly(thienylphenyl)amine; Dendritic polymer; Magnetic property; Spin concentration

1. Introduction

Dendritic or hyperbranched polymer structures with triarylamine derivatives, which provide interesting functions, e.g. energy transfer, light-harvesting antenna, organic high spin molecules and stepwise metal-assembling, have received attention as amorphous and soluble polymers [1–7]. Not only are the amorphous properties very interesting, but also the electronic and redox ones for the branched polymers. Carrier transport is an important factor contributing to the electronically conductive materials. The three-dimensional structure of a branched polymer might allow improved carrier transport to provide quite different electrical properties. In our previous reports, some novel types of oligo(thienylphenyl)amine derivatives having oligothiophene as the backbone moiety and thiophene as the terminal moiety were synthesized, and their electrochemical and photochemical properties were investigated.

We observed intra-molecular energy transfer from the terminal moiety to the backbone in the oligomers. The resulting oligomers showed significantly better redox properties and conductivity compared with the linear types, because the branched structure is advantageous for electron and hole transfers [8,9]. Moreover, when the oligomers were used for hole-transport and/or the emitting layers of organic light emitting diodes (OLED), the device that used more branched oligomers showed higher brightness and luminance efficiency than the others [10,11]. Also, we have already reported and demonstrated the unique metal assembling properties and hole-transporting material for OLEDs with novel synthesized phenylazomethine dendrimers having a tris(thienylphenyl)amine core. Moreover, oligo(thienylphenyl)amine derivatives that have different thiophene units and potential gradient molecules were synthesized and investigated as energy transfer models based on the thiophene units [3,7].

In this study, we synthesized poly(tris(thienylphenyl)amine)s with a dendritic structure (PTPA) and a linear type (PMeTPA) (Fig. 1) by the electro-oxidative...
polymerization of the tri-functional and two-functional monomers, respectively, and investigated their electrical and magnetic properties.

2. Experimental

2.1. Chemicals

All reagent grade chemicals were purchased from Aldrich, Kanto Kagaku Co., Inc., and Tokyo Kasei Co., Ltd, and were used without further purification. The supporting electrolyte was recrystallized before use.

2.2. Synthesis of monomers

The branched monomer, tris(4-(2-thienyl)phenyl)amine (TPA), was prepared by a cross coupling reaction using Grignard thiophene which was added to a solution of tris(4-bromophenyl)amine with a palladium catalyst in THF. The mixture was refluxed for 12 h, and quenched by adding saturated ammonium chloride. TPA was isolated by column chromatography as yellow needles after extracted with chloroform and dried over anhydrous sodium sulfate.

\[
\text{MS (FAB): } m/z = 491.
\]

\[
\begin{align*}
\text{\^1H NMR (C}_6\text{H}_4\text{D}_8\text{O): } & \delta = 7.03 \text{ (m, 3H), } 7.11 \text{ (d, 6H, } J_{\text{AB}} = 8.8 \text{ Hz), } 7.30 \text{ (m, 6H), } 7.55 \text{ (d, 6H, } J_{\text{AB}} = 8.7 \text{ Hz).} \\
\text{\^13C NMR (C}_6\text{H}_4\text{D}_8\text{O): } & \delta = 123.0, 124.7, 124.9, 127.1, 128.4, 130.1, 144.5, 147.2.
\end{align*}
\]

The linear monomer, 4-methylthienylphenyl-bis(4-thienylphenyl)amine (MeTPA), was prepared by a method similar to that mentioned above involving the reaction of the TPA monomer using 2-Grignard-5-methylthiophene to produce a yellowish powder.

\[
\text{MS (FAB): } m/z = 505.
\]

\[
\begin{align*}
\text{\^1H NMR (C}_6\text{H}_4\text{D}_8\text{O): } & \delta = 2.05 \text{ (s, 3H), } 6.72 \text{ (d, 1H, } J = 3.42 \text{ Hz), } 7.04 \text{ (d, 1H, } J = 3.42 \text{ Hz), } 7.06 \text{ (dd, 2H, } J = 5.13, 3.42 \text{ Hz), } 7.10 \text{ (d, 2H, } J_{\text{AB}} = 8.8 \text{ Hz), } 7.13 \text{ (d, 4H, } J_{\text{AB}} = 8.3 \text{ Hz), } 7.25 \text{ (m, 4H), } 7.45 \text{ (d, 2H, } J_{\text{AB}} = 8.8 \text{ Hz), } 7.50 \text{ (d, 4H, } J_{\text{AB}} = 8.3 \text{ Hz).}
\end{align*}
\]

2.3. Synthesis of polymers

The electro-oxidative polymerization of the monomers \((10^{-3} \text{ M}, M=\text{mole/dm}^3)\) was carried out by cyclic voltammetry on a Pt disk electrode \((\varnothing = 6 \text{ mm})\). The solution was a mixture of acetonitrile and dichloromethane, and tetrabutylammonium tetrafluoroborate (TBABF$_4$, 0.2 M) was used as the supporting electrolyte. The potential was swept from 0 to 1.1 V vs. Ag/Ag$^+$. PTPA: IR (KBr): 1597, 1533, 1493, 1320, 1289, 1267, 1180, 816, 790, 689 cm$^{-1}$. Calcd for \((\text{C}_{30}\text{H}_{19}\text{NS}_{3})_n\): C 73.62, H 3.89, N 2.86; Found C 73.1, H 3.88, N 2.81. PMeTPA: IR (KBr): 3007, 2985, 2886, 1542, 1436, 1326, 1295, 1269, 1185, 814, 779, 685 cm$^{-1}$. Calcd for \((\text{C}_{31}\text{H}_{21}\text{NS}_{3})_n\): C 73.92, H 4.20, N 2.78; Found C 73.8, H 4.08, N 2.69.

2.4. Measurement apparatus

The infrared spectrum was obtained using a Shimadzu FT-IR 8300 spectrometer (potassium bromide pellet). The \(^1\text{H}\) and \(^1\text{C}\) NMR spectra were measured using a JEOL 400 MHz FT-NMR (JMN 400) in THF-$d_8$. The MALDI-TOF mass spectra were measured by a Shimadzu-Kratos KOMPACT MALDI SEQ using dithranol as the matrix. The FAB mass spectra were measured using a Shimadzu mass spectrometer with benzyl alcohol as the matrix. The electrochemical synthesis was carried out in a conventional two-compartment cell under an N$_2$ atmosphere after N$_2$ bubbling for 30 min using an electrochemical work station (BAS Co., Ltd, Model 660). The ESR spectrum was recorded using a JEOL JES-RE3X ESR spectrometer (X-band, 9.4 GHz). The spin concentration was determined by integration of the ESR signal.

3. Results and discussion

3.1. Preparation of monomers

TPA was synthesized in 79% yield by reaction with tris(4-bromophenyl)amine and Grignard thiophene to prepare the branched polymer. To prepare the linear polymer, MeTPA was synthesized by a similar synthetic method for TPA using Grignard-5-methylthiophene in 15% yield as a monomer.
3.2. Electro-oxidative polymerization of monomers

The monomers TPA and MeTPA were efficiently electro-oxidative polymerized to receive the corresponding polymers using the cyclic voltammetric method in the applied potential range from 0 to 1.1 V vs. Ag/Ag\textsuperscript{+} in the monomer solution of acetonitrile-dichloromethane. The oxidation potentials at around 0.51 and 1.0 V are assigned to the radical cation formation of the amine and the thiophene. In fact, the potential sweeping around the first redox couple between 0 and 0.7 V vs. Ag/Ag\textsuperscript{+} results in the non-formation of polymer films because the redox couple corresponds to the amine moiety (N→e=N\textsuperscript{2+}). Fig. 2 shows the cyclic voltammograms (CV) of MeTPA during electro-polymerization when swept 15 times. The polymer growth on the electrode was confirmed by the increasing redox current during electro-polymerization by potential sweeping. The polymerization takes place at applied potentials above 1.0 V because the cation radical formed by the oxidation of the thiophene unit is the active species for the polymerization. The polymerization proceeds through the oxidative coupling of the thiophene rings. The resulting polymers were insoluble in common solvents such as THF, toluene, etc.

On the other hand, the conductivities of the polymers were 2.4 and 0.61 S/cm for PTPA and PMeTPA, respectively, using a microelectrode array [12]. The conductivity of the branched polymer was almost one order of magnitude higher than that of the linear one (Table 1). As the branched and linear polymers containing the triarylamine moieties are amorphous without a crystalline structure, the polymers are estimated to have a similar packing structure. Intra- and intermolecular hopping mechanisms of the carriers are not very different for the branched and linear polymers. In fact, the band gaps are almost similar for the branched and linear one because of their similar electronic absorption spectra attributed to the cation radical. However, the branched structure is advantageous for electron and hole transfers [2,13–15]. The higher conductivity of the branched polymer results in the formation of a larger amount of polymer with a significantly higher redox activity and catalytic activity for the electron transfer on the electrode.

3.3. Magnetic properties of polymers

The polymers were obtained as powders with the BF\textsubscript{4}\textsuperscript{−} doped state due to stopping the electro-oxidative polymerization at the amine oxidation potential although the normalized magnetization plots (M/M\textsubscript{S}) for both PTPA and PMeTPA are close to the Brillouin curves for S=1. This behavior indicates that the spin center is isolated in PTPA, but mutually interacts in PMeTPA leading to the triplet state (Fig. 3). The spin concentrations determined by the M\textsubscript{S}
values of PTPA and PMeTPA were 7.3–7.4 and 1.3–1.4%, respectively. The branched polymer of PTPA shows a much higher spin concentration than that of the linear polymer.

The solid ESR spectra of PTPA and PMeTPA at room temperature are shown in Fig. 3 inset. Strong ESR signals at \( g = 2.0027 \) and 2.0030 indicated the formation of a triphenylamine cation radical. The formed cation radicals were less delocalized structures that resulted from the line widths, \( D_{Hpp} = 0.39 \) and 0.61 mT than \( \pi \)-conjugated polymers [6,16]. The line width usually depends on the spin concentration, however, the PMeTPA showed a large width despite the small spin concentration due to the polymer structure (Table 1).

In general, the ESR intensity was proportional to the spin concentration of the molecules. As shown in Fig. 4, the intensity of the ESR was saturated by depending on the input power on the ESR measurement of the polymers. The saturation experiment suggests that the spin center of PMeTPA is different from that of PTPA.

According to Ovchinnikov’s rule, the generated spins offset each other in the poly(thienylphenyl)amines [17]. However, this spin–spin interaction exists in the polymers explained not by a through bond but by a through space [18,19]. The linear structure of PMeTPA enables close contact between the polymer chains.

4. Conclusions

Poly(tris(thienylphenyl)amine)s, which have a branched (dendritic) structure (PTPA), and the linear type (PMeTPA) were synthesized by electro-oxidative polymerization, and their electrical and magnetic properties investigated. The branched polymer PTPA exhibits a higher conductivity than that of the linear polymer (PMeTPA), although the normalized magnetization plots \( (M/M_0) \) for PTPA and PMeTPA are close to the Brillouin curves for \( S = 1 \). The spin concentration determined by the \( M_S \) values of the polymers, PTPA (7.3–7.4%) is much higher than that of PMeTPA (1.3–1.4%).

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