Preparation of Hole Transporting Polymers by Condensation Polymerization of Triphenylamine Derivatives

Hisaya Sato, Kenji Ogino, Hidenori Hirai

Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

SUMMARY: Hole transporting polymers were prepared by condensation polymerization of triphenylamine and N,N,N',N'-tetraphenylbenzidine (TPD) having alkyl group with aldehydes in the presence of *p*-toluenesulfonic acid. The obtained polymers had molecular weight higher than 10,000 and good film formation ability. It was found that the aromatic amine monomers were connected with aldehyde monomer at the *p*-position of the phenyl group. TPD-aldehyde polymers had almost the same UV absorption and redox potentials as those of TPD monomer indicating that the electronic structure of amine unit did not change by the polymerization. The hole transporting mobility was in the range of 10^{-3}-10^{-6}cm^2/Vs. The electroluminescent device consisting of ITO/TPD polymer/Alq/Mg-Ag had a maximum luminance of 9000 cd/m^2.

Keywords: triphenylamine, aldehyde, addition condensation polymerization, hole transporting,

Introduction

Hole transporting materials are used in the photosensitive dram of a copier or electroluminescent, photorefractive, or photochromic device. Triphenylamine (TPA) derivatives, especially N,N,N',N'-tetraphenylbenzidine (TPD), are most widely used hole transporting materials. Low molecular weight compounds are mainly used as a mixture in a polymer or vapor deposited thin film. However, the low molecular weight compounds had poor mechanical and thermal properties. Several attempts have been made to prepare polymers having TPD units in order to improve the poor properties of low molecular weight compounds. Some researchers prepared vinyl monomers and polymerized them by a radical or anionic initiator. Styrene, acrylate, or acrylamide type monomers were prepared using TPD having hydoroxy or amino groups [1-4]. Vinyl monomers in which vinyl group is directly attached to the aromatic ring was also prepared from TPA having formyl group [5]. Other attemps to prepare polymeric materials were intoroduction of two functional groups followed by polycondensation to prepare polymers [6,7]. However, monomers thus far prepared need

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introduction of one or two functional groups such as hydroxy, amino, or carbonyl groups to TPA derivatives. Since amino group is an activating group for electrophilic substitution of aromatic ring, it is expected that TPA derivatives can be used as a monomer without introduction of special functional groups.

In this paper hole transporting polymers were prepared by addition condensation reaction of TPD derivatives with aldehydes. The thermal, electrical, and electrochemical properties of the polymers were measured. Electroluminescent devices were prepared using the polymer as a hole transporting material and aluminum tris(quinolynol) as an electron transporting and emitting material.

Experimental

Materials

All the reagents were obtained commercially and used without further purification except otherwise mentioned. Chlorobenzene used for the solvent of polymerization was distilled over calcium hydride. Benzaldehyde (BA) and 4-butoxybenzaldehyde (BOBA) was distilled under reduced pressure before use.

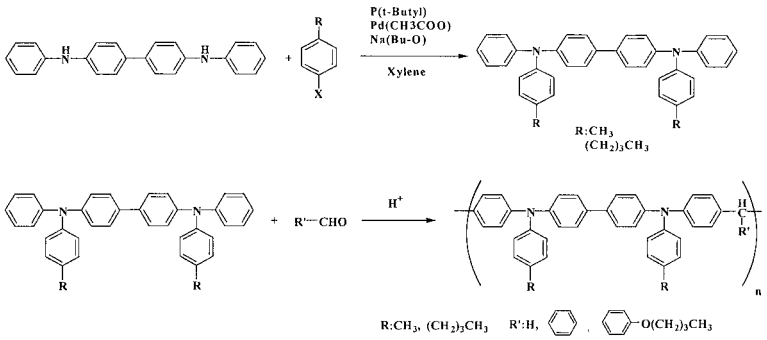
N,N'-bis(4-metylphenyl)-N,N'-diphenylbenzidine (MTPD) was prepared using Toso method [8] by reacting N,N'-diphenylbenzidine with 4-bromotoluene in the presence of palladium acetate and tri(t-butyl)phosphine catalyst and using sodium t-butoxide as a dehydrobrominating reagent. Xylene was used as a reaction solvent. The reaction was carried out at 130^0 C for 3 hours. The crude product was purified by column chromatography using silica gel as an stationary phase and toluene:hexane (1:1) as an eluent. Slightly yellow glassy material was obtained with a yield of 90%. H-1 NMR spectrum (in $CDCl_3$): 2.30 ppm [s, 6H, $-CH_3$] and 6.9-7.45 ppm [m, 26H, aromatic protons].

Similarly, N,N'-bis(4-butylphenyl)-N,N'-diphenylbenzidine (BTPD) was prepared by reacting N,N'-diphenylbenzidine with 4-bromobutylbenzene with a yield of 90%. H-1 NMR spectrum (in $CDCl_3$): δ from TMS; 0.95ppm [t, 6H, $-CH_3$], 1.38ppm [m, 4H, $-CH_2$], 1.60ppm [m, 4H, $-CH_2$], 2.58ppm [t, 4H, 4H, $-CH_2$] , 2.30ppm [s, 3H, $-CH_3$] , and 6.9-7.45 ppm [m, 26H, aromatic protons].

N-Tolyldiphenylamine (TDPA) was also prepared using Tosho method from diphenylamine and 4-bromotoluene with a yield of 80%. H-1 NMR ($CDCl_3$) δ from TMS: 2.30 ppm [s, 3H, -

CH_3] and 6.9-7.3 ppm [m, 14H, aromatic protons].

Polymerization was carried out under nitrogen atmosphere. Molecular weight was determined by GPC (eluent: chloroform) using a calibration curve for polystyrene. Reaction scheme is shown in Scheme 1.



Scheme 1. Synthesis of monomer and polymer

Measurements

NMR spectra were recorded on a chloroform-*d* solution at 50°C using a JEOL α-500 spectrometer (500 MHz for H-1). Glass transition temperature was measured by Rigaku Thermo DSC 8230 at the temperature increasing rate of 10K/min. UV absorption spectra were recorded on JASCO V-570 spectrophotometer in chloroform (10μg/ml). Cyclic voltammetry was carried out in a one-compartment cell with a polarization unit (TOHO PS-06). The measurement was conducted for the cast film on platinum working electrode and in dry acetonitrile containing tetra-n-butylammonium perchlorate. Platinum spiral was used as a counter electrode and Ag/AgCl as a reference electrode. Hole mobility was determined by a time-of-flight (TOF) method with a cell consisting of Al/Ti-phthalocyanine (Ti-Pc)/polymer/semitransparent gold and using xenon lamp. Electroluminescent device is constructed as follows: ITO glass was covered with polymer film with the thickness about 40-50 nm by spin coating, followed by the construction of Alq (50nm), SrO (0.5nm), and Al (150 nm) layers by vapor deposition.

Results and Discussion

1) Polymerization behavior

Since amino groups are activating group of the electrophilic substitution reaction of aromatic compounds, proton at the *p*- and *o*-positions of triphenylamine may be easily attacked by cationic species. As the reactivity of *o*-position is greatly reduced due to the steric hindrance, triphenylamine is considered to be a trifunctional monomer. Therefore, a bifunctional monomer can be obtained by introducing an unreactive group, such as alkyl or alkoxy group, to the *p*-position of one of the three phenyl groups in triphenylamine. It is well known that phenol reacts with formaldehyde in the presence of acid catalysts to yield novolac. By the analogy of phenol, which has an activating group of hydroxyl group, N-tolyldiphenylamine (TDPA) is expected to react with aldehydes to yield a linear polymer. TDPA was reacted with formaldehyde (FA) or benzaldehyde (BA) in the presence of *p*-toluenesulfonic acid. The reaction mixture became blue when the catalyst was added and became viscous as the reaction proceeded. The blue color was vanished when the reaction mixture was poured into acetone to precipitate the polymer. The results are shown in Table 1. TDPA reacted with FA to yield a polymer, which was insoluble in the reaction system and precipitated out. Only low molecular weight polymer was obtained. The polymer prepared with TDPA and BA was soluble in the solvent, therefore, the reaction proceeded homogeneously. High molecular weight polymer was obtained, when the molar ratio of aldehyde to amine was increased form 1.0 to 1.2.

Table 1. Results of Polymerization of TDPA with aldehydes*

Amine	Aldehyde[a]	Catalyst (mole%)	Temperature (°C)	Time (hr)	Yield (%)	Mn^b/ (10^4)	Mw^b/ (10^4)
TDPA	FA(1.0)	4	60	6	42	0.14	0.17
	(1.0)	4	80	6	66	0.22	0.42
	(1.0)	2	100	6	80	0.30	0.57
	BA(1.0)	4	80	6	70	0.24	0.40
	BA(1.2)	4	80	6	86	0.48	0.99
	(1.2)	4	100	9	88	0.92	2.23

*: Polymerization was carried out in chlorobenzene with the total monomer concentration of 2mol/l.

a: values in the parenthesis: mole ratio to amine.

b: determined by GPC

MTPD is considered to be a dimmer of TDPA and a bifunctional monomer having two phenyl groups and is estimated to have better hole transporting ability than TDPA due to the longer conjugation system. MTPD was reacted with FA, BA, or butoxybenzaldehyde (BOBA) using *p*-toluenesulfonic acid as a catalyst. Similar color change was observed in the reaction of TDPA. The results are listed in Table 2. In the case of MTPD polymers prepared with FA was soluble in the reaction system. MTPD is more reactive than TDPA and provided higher yield and higher molecular weight, when the reaction conditions were the same. Among the three types of aldehydes, FA was the most reactive and provided high molecular weight polymer with smaller amount of the catalyst (2 mole%) and shorter reaction time and at lower temperature (6 hours at 80°C). The increase of reaction time or reaction temperature produced a small portion of insoluble gel fraction.

Table 2. Results of Polymerization of MTPD and BTPD*

Amine	Aldehyde[a]	Catalyst (mole%)	Temperature (°C)	Time (hr)	Yield (%)	$Mn^b/(10^4)$	$Mw^b/(10^4)$
MTPD	FA(1.0)	4.0	60	6	86	0.87	1.27
	(1.0)	2.0	80	6	95	1.35	5.65
	BA(1.0)	4.0	80	6	81	0.77	1.30
	(1.0)	4.0	100	6	81	0.65	1.09
	(1.2)	4.0	100	3	99	2.07	12.1
	BOBA(1.2)	4.0	100	6	73	0.32	0.5
	(1.4)	4.0	100	6	80	0.61	1.03
	(1.4)	4.0	100	8	96	1.22	3.45
BTPD	B A(1.2)	4.0	100	3	98	1.27	4.22
	BOBA(1.4)	4.0	100	8	94	1.04	3.26

*: Refer to footnotes in Table 1.

BA was less reactive than FA and yield of acetone insoluble polymer was only about 80% even with the conditions in which FA provided almost quantitative yield. The increase of temperature only slightly affected yield and molecular weight. By increasing the mole ratio of aldehyde to MTPD from 1.0 to 1.2, molecular weight significantly increased. BOBA was less reactive than BA and provided only lower yield and molecular weight. By further increasing the mole ratio of BOBA to MTPD to 1.4, the yield increased to more than 90% and molecular weight to higher than 10^4. The low reactivity of BOBA can be explained by the interaction of ether oxygen with *p*-toluenesulfonic acid, which brought about the suppress of the catalytic

activity. Similar effect of oxygen was also observed for the polymerization in the solvent having oxygen atom [9].

BTPD showed almost the same polymerization reactivity as MTPD. All the polymers were soluble in usual organic solvents such as THF, chloroform, and toluene.

2) Structure of polymers

The structure of the polymer was determined by using H-1 NMR spectroscopy. The NMR signals were assigned by comparing the spectra of the monomer and polymer and also by considering the H-1 NMR of phenol-formaldehyde resin [10]. Figure 1 shows the H-1 NMR spectra of polymers prepared from MTPD with FA, BA, and butoxybenzaldehyde (BOBA).

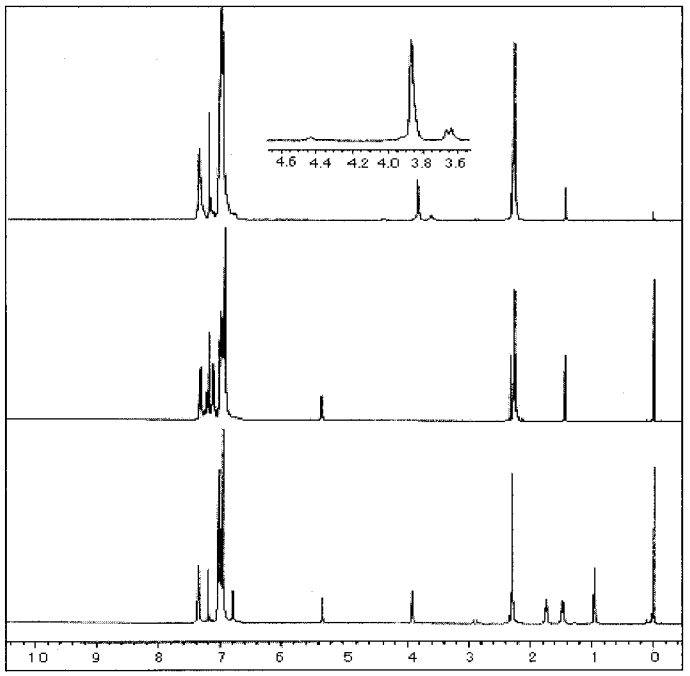


Figure 1. H-1 Spectra of MTPD-FA (above), MTPD-BA (middle), and MTPD-BOBA (below)

MTPD-FA polymer showed a methylene signal arising from FA unit at 3.84, which is assigned to methylene proton attached to 4-position of phenyl group in MTPD unit. A small signal at 3.63ppm is assigned to methylene proton attached to 3-position of 4-methylphenyl

group in MTPD. A smaller signal at 4.42ppm is assigned to methoxy group (Ph-C**H**$_2$-O- C**H**$_2$-Ph) arising from the reaction of two methylol groups. Therefore, it is concluded that FA unit is mainly linked at 4-position of phenyl with small amounts of other linkages. The presence of methylene linkage at 3-position of 4-methylphenyl group indicates that a part of MTPD acted as a tri- or tetrafunctional monomer, which lead to the formation of gel portion.

On the other hand, MTPD-BA polymer showed only one methine proton signal at 5.40 ppm, which are assigned to methine proton attached to 4-position of phenyl group. The absence of other type of linkage for the polymer with BA can be explained by the lower reactivity of BA monomer leading to higher selectivity and by the larger size leading to higher steric hindrance with methyl group in 4-methylphenyl unit. MTPD-BOBA polymer showed also only one methine proton signal in the residue of aldehyde unit and exhibited new signals due to the protons in butoxy group around 0.9, 1.5, 1.8, and 3.9ppm. Only one methine proton signal indicates that the MTPD units were exclusively linked with BOBA at the 4-position of phenyl group.

H-1 NMR spectra of polymers prepared with TDPA or BTPD were similar to the corresponding polymers prepared with MTPD. Therefore, it is concluded that triphenylamine monomers were exclusively linked at the 4-position of phenyl group when reacted with BA or BOBA, while small amount of other linkages were produced when reacted with FA.

3) Properties

The transition temperature was measured in a range of –20 to 250°C. The results are shown in the second column of Table 3. The glass transition temperature (Tg) of the polymers decreased in the order of MTPD-BA, MTPD-BOBA, BTPD-BA, and BTPD-BOBA, which indicates that the presence of long alkyl or alkoxy side chains decreased the Tg. All the polymers had higher Tg than monomeric TPD, which indicate that the polymer had better thermal stability than the monomer. The polymers prepared with FA were more brittle than those prepared with BA and did not provide good thick films. Polymers having long alkyl side chains had better processability and provided homogeneous films thicker than 20μm.

UV absorption was determined in chloroform solvent. All the polymers having TPD unit had two absorptions at about 320 and 360 nm with the molar absorption coefficients of 4.8-5.0 and 5.7-5.9x10^4, while MTPD had absorptions at 311 and 345 nm with the molar absorption

coefficients of 4.1 and $5.2x10^4$, respectively. The small bathochromic and hyperchromic effects of the polymer can be explained by the methine or methylene substitution.

Redox potential is one of the most important values for organic charge transporting materials. Redox potential was determined by cyclic voltammetry (CV) for a thin film on platinum electrode and using Pt wire as counter electrode and Ag/AgCl as a reference electrode. Figure 2 shows CV ahart. The color of the film changed from slightly yellow (neutral) to dark blue (positively charged). The redox signal became smaller as the increase of cycle due to the dissolution of the polymer. The color of the electrolyte changed to blue due to the dissolved charged materials. As shown in Table 3 all the polymers were found to have two oxidation potentials around 0.9V and 1.0V versus Ag/AgCl electrode. These values were almost equal to those of low molecular weight compound (MTPD). Therefore, it can be said that introducing TPD unit into the polymer chain does not significantly change its electronic properties.

Table 3. Properties of polymers

Polymer	Tg(°C)	λ_{max} (nm)	$\varepsilon_{max}(/10^4)$	Epa_1(eV)	Epa_2(eV)	Epc_1(eV)	Epc_2(eV)
MTPD-FA	183	319, 359	4.8, 5.7	0.87	0.93	0.81	0.90
MTPD-BA	239	319, 359	4.8, 5.7	0.90	0.96	0.84	0.93
MTPD-BOBA	203	319, 359	4.9, 5.8	0.88	0.93	0.80	0.89
BTPD-BA	180	319, 360	5.0, 5.9	0.90	0.93	0.82	0.86
BTPD-BOBA	163	319, 359	5.0, 5.8	0.90	0.93	0.84	0.91
MTPD	63	311,□354	4.1, 5.2	0.79	0.93	0.72	0.84

The values of ε_{max} indicates molar absorption coefficient for TPD unit.
Epa and Epc represent oxidation and reduction potentials, respectively.
Pt wire was used as working and counter electrodes and Ag/AgCl as reference electrode.

Hole mobility was measured by a time-of-flight method using the cell consisting of Al/Ti-phthalocyanine/polymer/semitransparent gold. MTPD-FA polymer was too brittle to provide film thicker than 10 μm suitable for TOF measurement. Other polymers provided thick films. Hole mobility was determined from the thickness of the film (d), applied voltage (V), and transit time (τ_{tr}), which was determined by the intersection of the two slopes, by using the following equation:

$$\mu = d^2 / \tau_{tr} V$$

In Figure 2 hole mobility was plotted against the square root of photocurrent. MTPD-BOBA had the highest mobility of $10^{-3}cm^2/Vs$. Other polymers exhibited hole mobility in the range of 10^{-4} and $10^{-3}cm^2/Vs$.

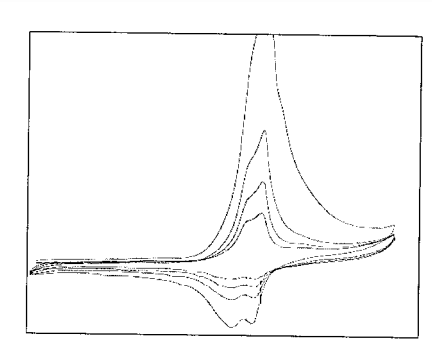


Figure 2. CV chart of MTPD-BA

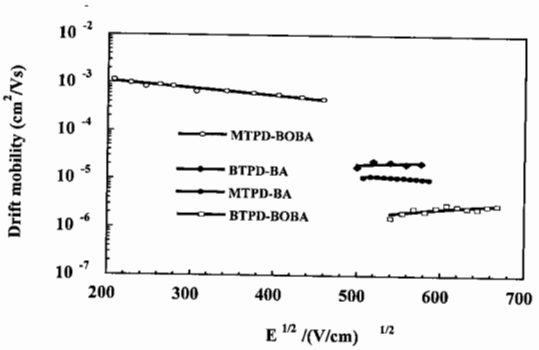


Figure 3. Drift Mobility of Polymers

4) Electroluminescent device

An electroluminescent device was constructed using MTPD-BOBA polymer as a hole transporting layer and Alq as an electron transporting and emitting layer. Figure 3 shows voltage-current-luminance relation of the device. The device had a turn-on voltage, the lowest applied voltage at which the luminance exceeds 1 cd/cm^2, at 5.2V and maximum luminance of $9000cd/m^2$. These values are almost equal to those of the device using MTPD as a hole transporting material.

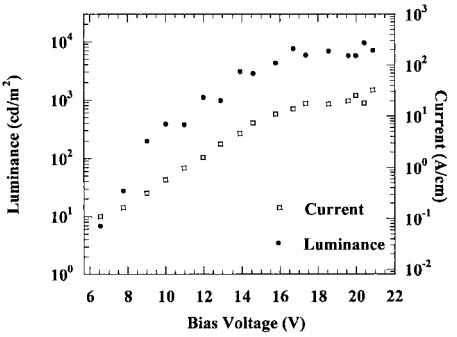


Figure 4. Current-voltage and luminance-voltage characteristics

Summary

Triphenylamine and N,N,N',N'-tetraphenylbenzidine (TPD) having alkyl group were reacted with aldehydes in the presence of *p*-toluenesulfonic acid to obtain polymers having triphenylamine units in the main chain. High molecular weight polymers were obtained with high yield. It was found that the aromatic amine monomers were predominantly connected with aldehyde monomer at the *p*-position of the phenyl group. TPD-aldehyde polymers had almost the same UV absorption and redox potentials as those of TPD monomer indicating that the polymers had almost the same electric properties as the low molecular weight compound. The hole transporting mobility was in the range of 10^{-3}-10^{-6}cm^2/Vs. The electroluminescent (EL) device consisting of ITP/TPD polymer/Alq/Mg-Ag had a maximum luminance of 9000 cd/m^2 and it was found that the polymers can be used as a hole transporting layer of EL device.

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