Preparation of 3,4-Ethylenedioxythiophene (EDOT) and N-4-butylphenyl-N,N-diphenylamine (BTPA) Copolymer Having Hole Transport Ability

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Abstract: Hole transport copolymers consisting of 3,4-ethylenedioxythiophene (EDOT) and N-4-butylphenyl-N,N-diphenylamine (BTPA) were synthesized by oxidative coupling reaction using $FeCl_3$ as an oxidant. These copolymers showed good solubility and their thin films showed sufficient morphological stability. The copolymers showed an absorption maximum around 320 nm. Copolymers had an oxidation peak at approximately 1.03~1.14 V versus the Ag/AgCl electrode. The hole mobility increased with increasing portion of the EDOT unit. The hole mobility of the copolymer containing 57% of the EDOT unit showed the highest mobility of 3×10^{-5} $cm^2/V \cdot s$.

Keywords: hole transport polymer, charge transport, oxidation polymerization, cyclic voltammogram, electro luminescence.

Introduction

It is known that 3,4-ethylenedioxythiophene (EDOT) provides a good polymer (PEDOT). However, PEDOT is insoluble in usual solvents and difficult to process by itself. PEDOT complex with poly(styrene sulfonic acid) (PSS) provides a suspension in water and used to prepare conducting film for electroluminescent device.[1] EDOT has only two hydrogen atoms that can be oxidized and thus can be considered as bifunctional monomer. Therefore, its poor solubility is considered to come from strong interaction with other molecules due and not from gel formation.[1-3]

Triarylamine derivatives, such as triphenylamine (TPA) and N,N,N',N'-tetraphenylbenzidine (TPD), have been extensively used as hole-transporting materials (HTMs) for photo-conductors and organic electroluminescent (EL) devices.[4-8] They have high hole-transporting abilities due to the fact that they are easily oxidized to form stable radical cation.[9-12] However, the low molecular weight compounds of TPA derivatives have problems such as the lack of the thermal stability and the mechanical strength.[4]

Recently, we reported that methyltriphenylamine can be polymerized in high yield by the chemical oxidative polymerization by using ferric chloride as an oxidant.[13] However, the molecular weight and solubility of the resulting polymers were not good enough to make a good thin film. It was

found that the introduction of bulky substituent in the side chain increased the solubility of polymer and increased the film formation property.[14,15]

In this study we investigated the copolymerization of 3,4-ethylenedioxythiophene (EDOT) and N-4-butylphenyl-N,N-diphenylamine (BTPA) to improve the solubility of EDOT. The optical and electrical properties of the copolymers were also measured and compared with homopolymers.

Experimental

Synthesis of Monomer (Scheme I). BTPA was prepared from diphenylamine and 4-bromobutylbenzene using palladium(II) acetate and tri(t-butyl) phosphine as a catalyst and sodium t-butoxide as a dehydrogenating reagent. The obtained compound was purified by column chromatography (silica gel/toluene-hexane: 1-3) followed by drying under reduced pressure. It was synthesized using already published procedures.[16]

EDOT was obtained commercially and used without further purification.

Polymerization (Scheme II). EDOT (100 mg, 0.70 mmol) and BTPA (212 mg, 0.70 mmol), and dehydrated solvent (5 mL) were in the flask under nitrogen atmosphere. To the monomer solution was added 456 mg (2.81 mmol) of $FeCl_3$. The reaction was terminated by pouring the reaction mixture into 100 mL of methanol containing small amount of p-toluene sulfonic acid. The precipitate was collected by

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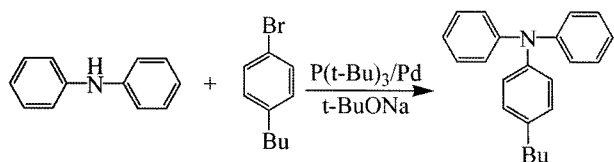
Scheme I. Synthetic route of *N*-4-butylphenyl-*N*,*N*-diphenylamine (BTPA).
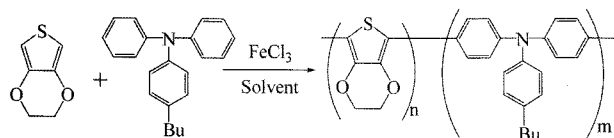
Scheme II. Synthesis of EDOT and BTPA copolymer.

filtration and washed with methanol. The obtained product was dissolved in chloroform and washed with disodium dihydrogen ethylenediamine tetraacetate dihydrate aqueous solution two times. The organic layer was separated, concentrated, and reprecipitated into methanol containing small amount of ammonia. The copolymer was dissolved in chloroform to separate insoluble part and reprecipitated in to methanol.

Measurement. ^{1}H NMR spectra were recorded on chloroform-*d* solution with tetramethylsilane (TMS) as an internal standard using a JEOL α-500 spectrometer. Average molecular weights of copolymers were estimated by gel permeation chromatography (GPC) using JASCO 880 pump and a JASCO UV-970 detector. Chloroform was used as an eluent, and the molecular weight was calibrated using polystyrene standards. UV absorption spectra were recorded on JASCO Ubest V-570 spectrophotometer in chloroform. Redox potentials were measured by cyclic voltammetry (CV) in a one-compartment cell with a polarization unit (TOHO PS-06). The measurement was conducted for the cast film on a platinum working electrode and in dry acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (Bu$_4$NClO$_4$) as an electrolyte under nitrogen atmosphere at the scanning

rate of 20 mV/sec. Platinum spiral wire was used as the counter electrode, and Ag/AgCl was used as a reference electrode. Hole drift mobility was determined by a time-of-flight (TOF) method with the device consisting of ITO/Ti-phthalocyanine/polymer/Al and xenon lamp. Film thickness was determined by a profilometer (DEKTAK, Solan).

Results and Discussion

Copolymerization of EDOT and BTPA was carried out with the monomer feed ratio of 1:1 using FeCl$_3$ as an oxidant. The results are tabulated in Table I. Chloroform solvent provided 5~15% higher yield than nitrobenzene solvent. However, the yield of insoluble part was higher for chloroform than nitrobenzene. The yield increased by the increase of the amount of oxidant, temperature, and reaction time. Increase of amount of oxidant and temperature also brought the increase of insoluble part. Soluble portion was soluble in common organic solvents such as toluene, chloroform, and tetrahydrofurane. These solubility of copolymers showed good films property. The highest yield with negligible insoluble portion was obtained with nitrobenzene solvent, FeCl$_3$ of 2 times of monomer, at room temperature (ca. 20 °C), and reaction time of 24 h.

The monomer feed ratio was changed with these reaction conditions. With these conditions no polymer was obtained from using only BTPA as a monomer. On the other hand, EDOT provided 78.9% yield, although soluble portion was only negligible. The yield decreased from 64.3 to 41.2% with the increase of EDOT feed from 50 to 75%. The yield increased after 80% of EDOT monomer feed. The number average molecular weight for the soluble portion was around 2 thousands regardless of the monomer feed ratio. The number average molecular weight is around 2 thousands. On the other hand, weight average molecular weight was higher than 100 thousands, showing large polydispersive index.

Table I. Copolymerization Conditions and Results^a of EDOT and BTPA

Solvent	FeCl$_3$/Mon.	Reaction Temperature (°C)	Reaction Time (h)	Yield^b (%)	M_n (×10^3)	M_w (×10^3)
Chloroform	2	r.t.	6	41.0 (19.1)	1.70	281
Chloroform	2.5	r.t.	6	64.4 (43.6)	1.81	254
Chloroform	2	40	6	60.8 (30.3)	1.79	240
Chloroform	2	r.t.	24	75.3 (25.3)	1.97	133
Nitrobenzene	2	r.t.	6	36.3 (0.0)	1.81	204
Nitrobenzene	2.5	r.t.	6	43.3 (22.8)	1.84	209
Nitrobenzene	2	40	6	49.7 (18.8)	1.88	180
Nitrobenzene	2	r.t.	24	64.3 (0.0)	1.96	155

^{a}Copolymerization conditions, EDOT and BTPA reaction was carry out with the monomer feed ratio of 1:1. ^{b}Values in parentheses denote insoluble part in chloroform.

Table II. Results of Copolymerization[a] of EDOT and BTPA (Comparative Monomer Feed Ratio)

EDOT in Feed (mole%)	Yield[b] (%)	M_n (×10³)	M_w (×10³)	EDOT in Polymer (mole%)
0	0.0 (0.0)	-	-	0
50	64.3 (0.0)	1.96	155	41
67	58.6 (3.8)	2.04	98	55
75	41.2 (10.8)	1.99	153	57
80	49.3 (45.5)	1.88	93	-
100	78.9 (78.9)	4.89	129	100

[a]Copolymerization conditions, solvent: nitrobenzene, FeCl₃ : 2 times of monomer reaction temp.: room temp., reaction time : 24 h. [b]Values in parentheses denote insoluble portion in chloroform.
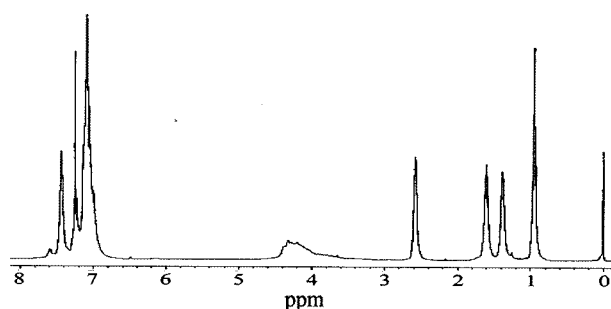

Figure 1. ¹H NMR spectra of copolymer (EDOT unit of 41 mole%).

Figure 1 shows the ¹H NMR spectrum of the copolymer obtained with the monomer feed ratio of 1:1, copolymer containing 41 mole% of EDOT unit. Aliphatic proton due to butyl group in BTPA unit appeared in the region of 1~3 ppm as four peaks. Ethylene proton in EDOT unit resonated around 4.2 ppm. In the region of 6.8~7.7 ppm appeared aromatic proton signal in BTPA unit. Signal around 6 ppm, the proton signal of the thiophene unit disappeared. The percentage of EDOT unit in the copolymers was determined from the area ration of the peaks around 4.2 and 0.1~2.7 ppm. The percentage of EDOT unit in the copolymer is shown the last column of the Table II.

EDOT fraction was 41 and 55% when the feed EDOT was 50 and 67%, respectively, which indicates that EDOT monomer is less reactive than BTPA (about 80%). Copolymerization with 75% of EDOT feed provided large portion of insoluble polymer and EDOT unit in the soluble portion was only 57%. Analysis of IR spectra revealed that the EDOT unit of insoluble portion was larger than soluble portion, which indicates that the EDOT fraction differed greatly among the molecules and higher EDOT fraction polymer became insoluble.

Figure 2 shows UV-vis spectra of the obtained copolymers. PEDOT was treated with super sonic wave to solubilize, because PEDOT contained insoluble fraction. BTPA and EDOT showed absorption maxima around 260 and 305 nm.
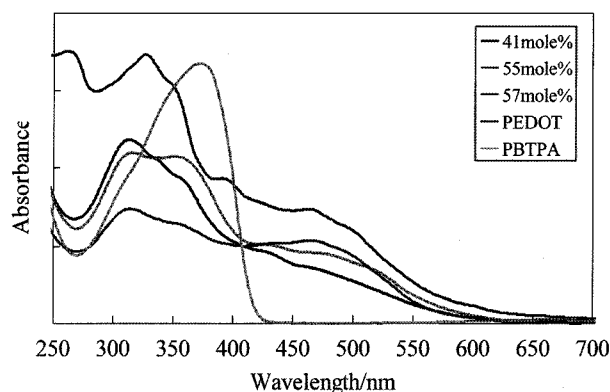
Figure 2. UV spectra of copolymers (EDOT mole% in polymer) and homopolymers.

Poly(N-4-butylphenyl-N,N-diphenylamine) (PBTPA) had absorption maximum around 380 nm. PEDOT showed absorption around 270, 330, and 460 nm. PEDOT has a longer conjugation consisting of only aromatic-aromatic linkage, while PBTPA had a shorter conjugation because conjugation was terminated at nitrogen. Therefore, absorption around 460 nm and higher may be attributed to the longer conjugation of EDOT units. The copolymers also had absorption around 460 nm, which is characteristic of EDOT unit with a longer conjugation.[17]

The redox potential was measured by CV. All the polymers showed oxidation peak. PBTPA had oxidation peak around 1.12 V versus Ag/AgCl electrode and that of EDOT-BTPA copolymer was lower; 1.03~1.14 V. HOMO level was calculated from oxidation potential. The copolymer with EDOT unit of 57% showed oxidation peak at 1.14 V.

The band gap was determined from the cut-off point of UV-vis absorption spectra. The LUMO level was calculated from HOMO and band gap. The HOMO and LUMO levels are listed in Table III.

The hole drift mobility of copolymers was measured by standard time-of-flight method. The mobility, μ, was calculated according to the following equation:

$$\mu = L^2 / t_T V$$

Where L is the sample thickness, t_T is the transit time, and V is the applied voltage. Transit time is determined from log i (current) vs. log t (time) plots. As shown in Figure 3, mobility

Table III. Results of CV and HOMO-LUMO Level

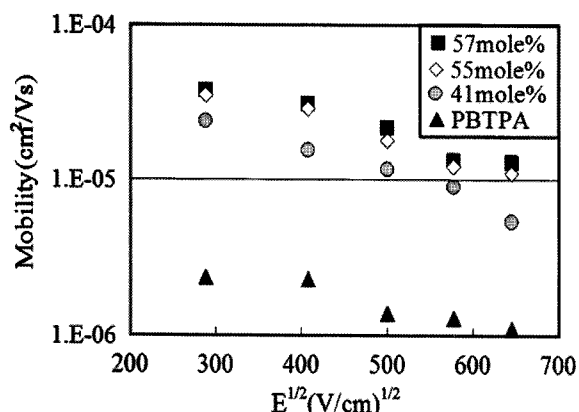| EDOT in Polymer (mole %)	E_{pa} (V)	E_g (eV)	HOMO (eV)	LUMO (eV)
0	1.12	2.98	-5.84	-2.86
41	1.03	2.15	-5.75	-3.60
55	1.08	2.07	-5.80	-3.73
57	1.14	2.20	-5.86	-3.66

Figure 3. Drift mobility of EDOT and BTPA copolymers (EDOT mole% in polymer).

increased with the increase of portion of EDOT unit.

Conclusions

Copolymerization of EDOT and BTPA was carried out using $FeCl_3$ as an oxidant. The best polymerization results, i.e., high yield with negligible insoluble portion was obtained when oxidant/monomer = 2, at 20 °C (r.t.) using nitrobenzene as a solvent. The obtained copolymer was soluble in common organic solvent such as toluene, chloroform, and THF. The copolymer showed absorption maximum around 320 nm. Copolymers had oxidation peak around 1.03~1.14 V versus Ag/AgCl electrode. Hole drift mobility of the copolymer containing 57% of EDOT unit showed highest mobility of 3×10^{-5} cm²/V·s.

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