A Novel Transparent Polyacetylene Bearing a Triphenylamine Moiety Prepared with a [Rh(norbornadiene)Cl]$_2$ Catalyst

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Summary: Novel soluble polyacetylenes having a triphenylamine moiety were synthesized by a [Rh(norbornadiene)Cl]$_2$ catalyst under quite mild conditions in fairly high yields. The obtained polymer showed to have *trans-transoid* sequence as the major main-chain structure which was generated through the so-called *cis*-to-*trans* isomerization was already induced even during the polymerization. The HCl doping of the polymer was resulted in the formation of the oxidized polymer where the so-called polaron or bipolaron was produced. In addition, we found that in the case of the pristine polymer unpaired electrons mainly localized on the triphenylamine moiety as the side chain. On the other hand, after the doping the unpaired electron delocalized on the main chain of the polymer.

Keywords: conjugated polymer; ESR; organometalic catalyst; polyacetylenes solid state structure

Introduction

Aromatic polyacetylenes such as poly(phenylacetylene) and its derivatives are potentially important materials from not only a scientific point of view, but also possible technological applications, e.g., photoconductor,[1–3] ferromagnetism,[4] gas permeability,[5–8] humidity sensor,[9,10] nonlinear optics (NLO),[11–15] and organic light emitting diodes (OLEDs),[16,17] and so on.

Previously, we have demonstrated that monosubstituted acetylenes such as phenylacetylene derivatives can be stereoregularly polymerized using a [Rh(NBD)Cl]$_2$, (NBD = norbornadiene) catalyst to selectively afford the corresponding polyacetylenes bearing a *cis-transoid* structure in high yields under quite mild conditions.[18–31] We also reported that triethylamine (TEA) or alcohol solvent effectively works as the cocatalyst in the polymerization.[29–31]

Recently, polyacetylenes having organic optics or electronics materials such as carbazole[32–46] and/or thiophene[47,48] unit as the side chain have been prepared. In this article, therefore, we report preparation of the novel polyacetylenes bearing the triphenylamine moiety as the side chain which have been well-known as splendid electroluminescence materials as hole transporting function[49–53] using the Rh complex catalyst (see Scheme 1) together with detailed characterization of the polymers obtained before and after HCl doping using ^{1}H NMR, electron spin resonance (ESR), and UV-Vis-near IR (UV-Vis-NIR) methods.

Experimental

Materials

The monomer, bis(4-butoxyphenyl)-(4-ethynylphenyl)amine, BBEA, was prepared according to equations shown in Scheme 2. [Rh(NBD)Cl]$_2$, was used

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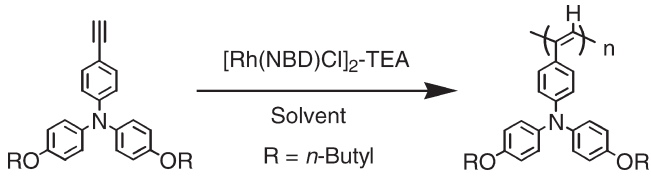


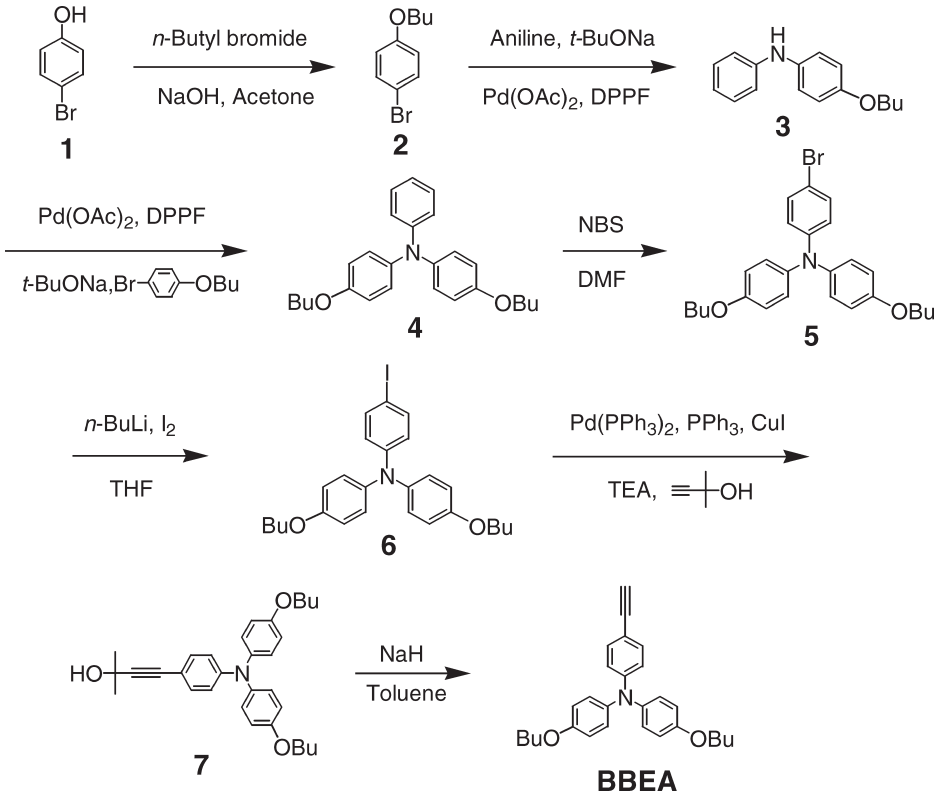
Scheme 1.
Polymerization of bis(4-butoxyphenyl)-(4-ethynylphenyl)amine, BBEA.

without further purification. Polymerization solvents were dried before use.

Monomer Synthesis

4-Butoxybromobenzene (2)
4-Bromophenol (1) (22.0 g, 0.10 mol) and sodium hydroxide (14.8 g, 0.37 mol) were dissolved in acetone (300 mL) and refluxed for 1 hr. *n*-Butyl bromide was added to the mixture and refluxed for 6 hrs. To the resulting solution, diethyl ether was added to extract the product, and the product was washed three times with water. The obtained organic layer was dried with anhydrous magnesium sulfate for 1 hr, filtrated, and purified by column chromatography on silica gel using *n*-hexane. The product, 4-butoxybromobenzene (2) was obtained in 20.6 g, 0.09 mol, yield: 90%.

(4-Butoxyphenyl)phenylamine (3)
The obtained 4-butoxybromobenzene (2) (27.5 g, 0.12 mol), palladium acetate (0.5 g, 2.6 mmol), and diphenylphosphinoferrocene (DPPF) (4.0 g, 7.2 mmol) were



Scheme 2.
Synthetic route of BBEA.

dissolved in dried toluene (300 mL) and stirred under nitrogen at 70 °C for 1 hr. Aniline (14.9 g, 0.16 mol), and sodium *tert*-butoxide (15.4 g, 0.16 mol) were added and stirred at 100 °C for 50 hrs. To the resulting solution, diethyl ether was added to extract the product, and the product was washed three times with water. The obtained organic layer was dried with anhydrous magnesium sulfate for 1 hr, filtrated, and purified by column chromatography on silica gel using chloroform. The product, bis(4-butoxyphenyl)phenylamine (3) was obtained in 27.5 g, 0.114 mol, 95%.

Bis(4-butoxyphenyl)phenylamine (4)

4-butoxybromobenzene (2) (34.0 g, 0.15 mol), palladium acetate (1.0 g, 5.2 mmol), and diphenylphosphinoferrocene (DPPF) (6.0 g, 11.0 mmol) were dissolved in dried toluene (300 mL) and stirred under nitrogen at 70 °C for 1 hr. (4-butoxyphenyl)phenylamine (3) (27.6 g, 0.11 mol), and sodium *tert*-butoxide (11.5 g, 0.12 mol) were added and stirred at 100 °C for 50 hrs. To the resulting solution, diethyl ether was added to extract the product, and the product was washed three times with water. The obtained organic layer was dried with anhydrous magnesium sulfate for 1 hr, filtrated, and purified by column chromatography using chloroform and purified by column chromatography using ether/hexane = 1v/2v. The obtained product, bis(4-butoxyphenyl)phenylamine (4) was obtained in 36.4g, 0.09 mmol, 85%.

(4-Bromophenyl)bis(4-butoxyphenyl)amine (5)

Bis(4-butoxyphenyl)phenylamine (4) (36.6 g, 94.0 mmol) was dissolved in *N*, *N*-dimethylformamide (DMF) (40 mL) without light and stirred under nitrogen. *N*-bromosuccineimide (NBS) (16.7 g, 94 mmol) in DMF (50 mL) solution were added and stirred at room temperature for two days. To the resulting solution, diethyl ether was added to extract the product, and the product was washed three times with water. The obtained organic layer was dried with anhydrous magnesium sulfate for 1 hr, filtrated, and purified by column chromatography on silica gel using chloroform. The product, (4-bromophenyl)bis(4-butoxyphenyl)amine (5) was obtained in 42.3 g, 90 mmol, 96%.

(4-Iodophenyl)bis(4-butoxyphenyl)amine (6)

(4-bromophenyl)bis(4-butoxyphenyl)amine (5) (23.0 g, 50.0 mmol) was dissolved in dried tetrahydrofuran (THF) (200 mL) and stirred under nitrogen at −78□. *n*-Butyllithium in *n*-hexane solution of 2.6 mol/L (30mL) was added and stirred at −78□ for 1hr. Iodine (12.6 g, 50.0 mmol) in dried THF (100 mL) solution was added and stirred at room temperature for 3 hrs. To the resulting solution, chloroform was added to extract the product, and the product was washed three times with water. The obtained organic layer was used without purify. The product, (4-iodophenyl)bis(4-butoxyphenyl) amine (6) was obtained in 23.5 g, 46 mmol, 91%.

4-{4-[Bis(4-butoxyphenyl)amino]phenyl}-2-methyl-3-butyne-2-ol (7)

(4-iodophenyl)bis(4-butoxyphenyl)amine (6) (23.4 g, 45.0 mmol), triphenylphosphine (1.0 g, 3.8 mmol), copper iodine (0.5 g, 2.6 mmol), dichlorobistriphenylphosphine-palladium (1.0 g, 1.4 mmol) were dissolved in triethylamine 100 mL and stirred under nitrogen at room temperature for 1 hr. 2-methyl-3-butyn-2-ol (5.7 g, 68.0 mmol) was added and stirred at 40 °C for 20 hrs. To resulting solution, dichloromethane was added to extract the product, and the product was washed three times with water. The obtained organic layer was dried with anhydrous magnesium sulfate for 1 hr, filtrated, and purified by column chromatography on silica gel using ether/hexane = 1v/1v. The product, 4-{4-[bis(4-butoxyphenyl)amino]phenyl}-2-methyl-3-butyne-2-ol (7) was obtained in 15.1 g, 32 mmol, 71%.

Bis(4-butoxyphenyl)-(4-ethynylphenyl)amine (BBEA, Monomer)

Sodium hydride (4.3 g, 0.18 mol) was dissolved in dried toluene (100 mL) and stirred under nitrogen for 1 hr. 4-{4-[bis(4-

butoxyphenyl)amino]phenyl}-2-methyl-3-butine-2-ol (7) (15.1 g, 32 mmol) in dried toluene (250 mL) solution was added and stirred at 100 °C for 3 hrs. The obtained organic layer was dried with anhydrous magnesium sulfate for 1 hr, filtrated, and purified by column chromatography on silica gel using ether/hexane = 1v/20v. The product, bis-(4-butoxyphenyl)-(4-ethynylphenyl)amine (BBEA, monomer) was obtained in 5.0 g, 12 mmol, 38%.

Polymerization

Polymerization was carried out using a U-type glass ampule equipped with two inlets capped with septum rubbers.[25,31] A typical polymerization procedure is as follows: $[Rh(NBD)Cl]_2$ (3.3 mg, 7.3×10^{-3} mmol) together with TEA as cocatalyst (20 μL), and the monomer (0.3 mg, 7.3 mmol) were placed in each side of the ampule, and polymerization solvent (7.3 mL) was also introduced to both sides of the ampule. The ampule was evacuated at ca. 10^{-2} Torr at −78 °C. After standing the solutions for 10 min, the monomer solution and the catalyst solutions were mixed in order to start the polymerization at the polymerization temperature. After 2 hrs the resulting polymer solution was poured into a large amount of methanol to precipitate a red or orange fiber product, filtrated, and dried *in vacuo* at *ca.* 10^{-3} Torr for 24 hrs at room temperature.

Characterization

The number average molecular weight (*M*n) and the molecular weight dispersity (*M*w/*M*n) of the resulting polymers were estimated by JASCO 900 gel permeation chromatography (GPC) equipped with a refractive index detector using chloroform as an eluent at flow rate of 0.5 mL/min with a Shodex K-806L column and calibrated with polystyrene standards (see Table 1). ^{1}H NMR spectra were recorded on a JEOL JNM-A 400 MHz using $CDCl_3$ as solvent at room temperature. UV-Vis-NIR spectra were recorded on JASCO V-570 using tetrahydrofuran (THF) as a solvent at room temperature. ESR spectra were observed on a JEOL FE1XG with 100 kHz field modulation at room temperature and 77 K.

HCl Doping

HCl doping procedure is as follows: After PBBEA (Table 1, run 6) (20 mg, 4.8×10^{-2} mmol) was dissolved in dried THF (20 mL) followed by addition of methanol solution of hydrochloric acid (Tokyo Kasei, 15 Volume%) (1 mL). The resulting mixture was stirred without light under nitrogen at room temperature for 3 hrs.

Results and Discussion

Polymerization

Table 1 shows the polymerization results of the polyacetylenes having the triphenylamine moiety prepared with the catalyst. The resulting polymers, PBBEAs were soluble in organic common solvents such as $CHCl_3$ and THF but insoluble in methanol. TEA may promote dissociation of the dimeric catalyst in order to generate a monomeric species associating with the added solvent like THF. The *M*n and *M*w/

Table 1.
Polymerization results of BBEA using a $[Rh(norbornadiene)Cl]_2$ catalyst.[a]

Run	Solvent	Temp. (°C)	Yield (%)	Mn[b]	Mw/Mn[b]	Color
1	TEA	−5	92	157,000	1.6	Red
2	TEA	30	90	190,000	1.3	Red
3	TEA	60	91	70,000	2.1	Red
4	Toluene	30	91	184,000	1.3	Red
5	THF	30	72	83,000	2.3	Orange
6	$CHCl_3$	30	91	203,000	2.6	Orange

[a] [M] = 0.1 mol/L; Polymn. Time = 2 hrs.
[b] Measured using GPC in $CHCl_3$ as an eluent and polystyrene as a standard.

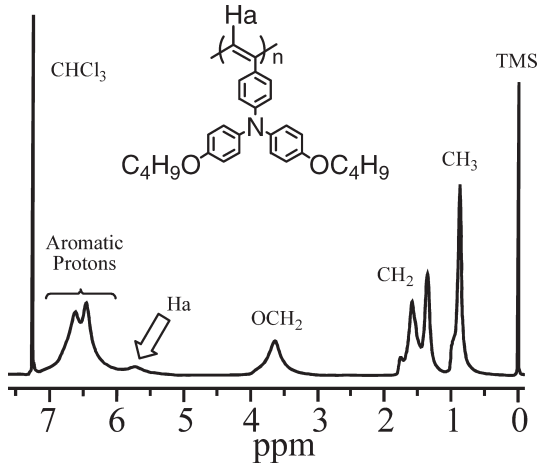


Figure 1.
^{1}H NMR spectrum of pristine Poly[bis(4-butoxyphenyl)-(4-ethynylphenyl)amine], PBBEA (Table 1. Run 6) observed in $CDCl_3$ at room temperature.

*M*n were estimated as *ca.* 70,000–203,000 and 1.3–2.6, respectively, and the polymer yields were estimated as around 72–92%.

^{1}H NMR

Figure 1 shows the ^{1}H NNR spectrum of the PBBEA (Table 1. run 6) observed in chloroform solvent at room temperature. Three singlet peaks observed at *ca*. 0.8, 3.6 and 5.8 ppm were ascribed to those of $-CH_3$ (6H), $-OCH_2-$ (4H), and =C–H (1H) in the polymer, respectively. Multiplet peaks observed at *ca*. 1.5 and 6.5 ppm were also assigned to $-CH_2CH_2-$ (8H) protons of the alkoxy side chain and aromatic protons (12H) of the triphenylamine moiety, respectively. Interestingly, all peaks were broadened and the peak due to main chain proton, =C–H was not clearly observed at *ca*. 5.8 ppm. These phenomena can be interpreted in terms of incorporation of the trans isomer sequence in the main chain suggesting that the so-called *cis*-to-*trans* isomerization was already induced even during the polymerization. This also implies that content of *trans* isomers is much higher than that of *cis* isomers. Such similar spectra have been observed in the case of monosubstituted polyacetylenes which were prepared with the so-called methathesis catalysts or thermal-treated polyacetylenes.[54] The observed line broadening may be interpreted by the so-called dipole-dipole magnetic interaction between the unpaired electrons and the protons in the *cis* and *trans* isomers, although slow molecular motion of trans isomers observed in the chloroform solution may be correlated.

ESR Spectra

ESR spectra were observed in order to investigate the effect of HCl doping against PBBEA (Table 1. run 6). Table 2 shows the ESR spectral parameters of the PBBEA polymer coating films obtained before and after HCl doping. The ESR parameters were estimated as $g = 2.0033$ and line width, $\Delta H_{msl} = 9.31$ G at room temperature and $g = 2.0030$ and $\Delta H_{msl} = 10.6$ G at 77 K, respectively. These data support that the PBBEA is composed of the *trans* isomers as the major component, because the observed line width is narrower than that of ordinary monosubstituted polyacetylenes having *cis* form as the case of poly(*p*-substituted)phenylacetylenes[48] prepared with the Rh complex catalyst. The observed g value also indicates that unpaired electron can localize at the N atom of the triphenylamine moiety,

Table 2.
ESR Parameters of Polymer coating film observed before and after HCl doping at room temperature for 3 hrs.

	Temp.	g value	ΔH_{msl} (Gauss)	Spin Conc.[a] (spins/g)
Before	r.t.	2.0033	9.3	1.02×10^{18}
	77 K	2.0030	10.6	—
After	r.t.	2.0026	12.4	3.42×10^{18}
	77 K	2.0028	13.8	—

[a] Spin Concentration was referred to Ultramarine Blue.

because the N as the heteroatom has a relatively large spin-orbit coupling constant, ζ,[55] compared with that of H or C atoms. On the other hand, the ESR parameters of the polymer coating film observed after HCl doping were determined as $g = 2.0026$ and $\Delta H_{msl} = 12.4$ G at room temperature and $g = 2.0028$ and $\Delta H_{msl} = 13.8$ G at 77 K, respectively, together with increase of the spin concentration from 1.02×10^{18} spins/g to 3.42×10^{18} spins/g. These results suggest that before the doping unpaired electrons localized at the N atom in the side chain to some extent. Thus, it is concluded that after the doping unpaired electrons localized in the main chain to show the typical hydrocarbon radicals as mentioned above.

UV-Vis-NIR Spectra

Figure 2 shows the UV-Vis-NIR spectra of polymer (Table 1. run 6) observed before and after HCl doping using THF solution at room temperature. A large peak having a shoulder at *ca.* 420 nm was observed at *ca.* 300 nm before the HCl doping. The shorter wavelength absorption at *ca.* 300 nm was assigned to the triphenylamine moiety, and the shoulder peaks at *ca.* 420 nm was ascribed to that of the main chain sequences. Interestingly, a broad peak at a fairy longer wavelength was observed after the HCl doping, whose absorption was extended to *ca.* 1400 nm. These data suggest that the so-called polaron or bipolaron are produced by one or two-electrons oxidation of the triphenylamine moiety through the HCl doping of main chain. This consideration is not inconsistent with the ESR parameters results above mentioned. It is noteworthy that the spectral intensity from *ca.* 450 to 750 nm is very low compared with those of *ca.* 325 ~ 450 nm and *ca.* 700 ~ 1300 nm. This result may mean that the HCl doped polymer can be classified as one of transparent polymer in the range of *ca.* 450 ~ 700 nm.

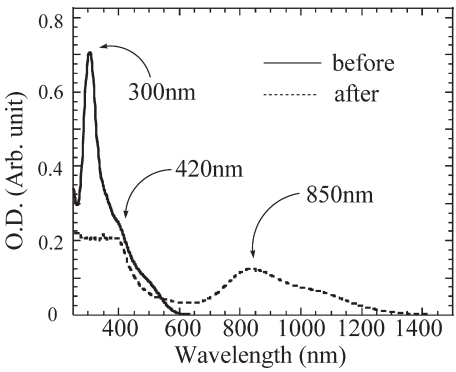


Figure 2.
UV-Vis-NIR spectra of PBBEA (Table 1. Run 6) in THF solution observed before and after HCl doping.

Conclusion

Bis(4-butoxyphenyl)-(4-ethynylphenyl)amine, BBEA, was successfully polymerized using a $[Rh(norbornadiene)Cl]_2$ catalyst in the presence of triethylamine as the polymerization solvent to produce the corresponding polymers in fairly high yields. The resulting polymers obtained before and after HCl doping were characterized in detail using ^1H NMR, ESR, and UV-Vis-near IR methods. Consequently, the resulting polymers were found to be composed of *trans* forms as the major component.

Interestingly, the polymer doped using HCl was found to be oxidized in order to produce the so-called polaron or bipolaron. In addition, we found that in the case of pristine polymer unpaired electrons localized on the triphenylamine moiety as the side chain. On the other hand, after doping the unpaired electron delocalized on the main chain of the polymer. Further, the doped polymer can be classified as one of the transparent polymer.

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