

Synthesis and Electrical Properties of Poly(1,4-diethynyl-2,5-dibutoxybenzene)

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ABSTRACT: Poly(1,4-diethynyl-2,5-dibutoxybenzene), a polymer containing diacetylene group in the main chain, was synthesized by oxidative coupling polymerization. This polymer was confirmed to have relatively high molecular weight and expected to have polydiyne structure without defects. In solid state ^{13}C NMR spectrum of this polymer, the peaks assigned to phenyl carbons were splitted to doublet because there were any kinds of conformation around the single bonds between triple bonds of diacetylene groups. A DSC curve of the polymer indicated that it was cross-linked at 620 K because of starting of the rotation around the single bond. Although conductivity of the polymer was very low, the polymer exhibited relatively high photoconductivity attributed to the nature of the repeating unit.

KEY WORDS Poly(1,4-diethynyl-2,5-dibutoxybenzene) / Conjugated Polymer / Oxidative Coupling Polymerization / Solid State CP/MAS ^{13}C NMR / Solid State Structure / Main Chain Conformation / Thermal Reactivity / Photoconductivity /

Diacetylene compounds are attracting increasing attention worldwide.¹ The reason for this interest is that these compounds are polymerized in solid state and afford single crystal polymers. Since the pioneering work of Wegner in late 1960's,² there have been many studies on the polymerization process³ and the physics of quasi-one-dimensional materials.⁴ Many kinds of applications were studied, such as conductive materials⁵ and nonlinear optical devices⁶ by using unique conjugated main chain of the polymers.

Hay reported that *m*-diethynylbenzene was polymerized to polydiyne by oxidative coupling polymerization,⁷ and the polymers with diacetylene groups have been investigated for thermal and optical curing materials. Recently, Lando and coworkers reported that poly(1,8-nonadiyne) which has alkylene spacer exhibited thermochromism and solvatochromism at-

tributed to the change of the main chain conformation.⁸ Whitesides and coworkers investigated thermal curing of soluble polydienes.⁹

In this paper, poly(1,4-diethynyl-2,5-dibutoxybenzene) (PDEDDB), which was a soluble all aromatic polymer, was synthesized and was investigated about its solid state structure. It was found that the main chain of the polymer was not highly conjugated because of the rotation of the single bonds in diacetylene groups, and the polymer exhibited low conductivity. However, the polymer had relatively high photoconductivity due to the nature of repeating units.

EXPERIMENTAL

Synthesis of a Monomer

1,4-Dibutoxybenzene (I). A solution of

hydroquinone (11 g, 0.1 mol) and *n*-butyl bromide (41.1 g, 0.3 mol) in 300 ml of 50% NaOH aqueous solution was refluxed for 8 h under nitrogen. The reactant was extracted with methylene dichloride (300 ml \times 3). The extract was dried over Na_2SO_4 and evaporated. The residue was recrystallized from methanol. White platelet crystal of 16.0 g was obtained (yield 72%). ^1H NMR (in CDCl_3) δ 1.0 (t, 6H, CH_3), 0.5 and 1.7 (m, 8H, CH_2), 3.9 (t, 4H, OCH_2), 6.8 ppm (s, 4H, aromatic).

1,4-Dibromo-2,4-dibutoxybenzene (2). **1** (11 g, 50 mmol) was dissolved in dry CCl_4 and bromine (19.2 g, 120 mmol) was added to the solution dropwise for 30 min. The mixture was stirred at 40°C for 4 h. After removing excess bromine by nitrogen bubbling, the reactant was evaporated and recrystallized from methanol. White powder of 16.0 g was obtained (yield 80%). ^1H NMR (in CDCl_3) δ 1.0 (t, 6H, CH_3), 1.5 and 1.7 (m, 8H, CH_2), 4.0 (t, 4H, OCH_2), 7.1 ppm (s, 2H, aromatic).

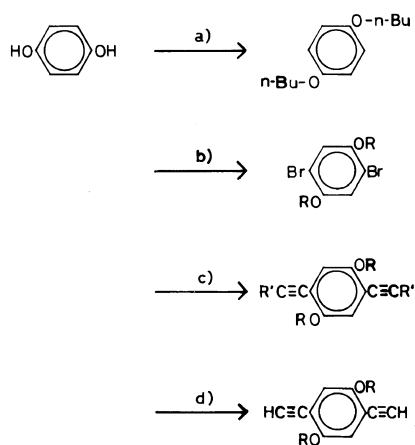
1,4-Diethynyl-2,4-dibutoxybenzene (3). This compound was synthesized by the method reported by Hagihara *et al.*¹⁰ **3** (7.6 g, 20 mmol), trimethylsilylacetylene (4.8 g, 48 mmol), 500 mg of cuprous chloride, and 500 mg of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ were dissolved in 200 ml of dry piperidine. The solution was stirred at 40°C for 1 day under nitrogen and was evaporated. The residue was dissolved in 100 ml of toluene and was passed through a short silica gel column. After removal of solvent, the reactant was dissolved in methanol containing 20 ml of 1 *N* aqueous potassium hydroxide solution and was stirred for 1 day. The product was extracted with ether and was purified by column chromatography on alumina (eluent: benzene-hexane, 1:9). Recrystallization from methanol afforded yellow powder of 2.8 g (yield 52%). mp 102.5°C . ^1H NMR (in CDCl_3) δ 1.0 (t, 6H, CH_3), 1.5 and 1.8 (m, 8H, CH_2), 3.3 (s, 2H, $\equiv\text{CH}$), 4.0 (t, 4H, OCH_2), 7.0 ppm (s, 2H, aromatic).

An absorption at 860 cm^{-1} in IR spectrum of **3**, which was assigned to isolated proton of

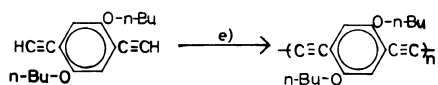
phenyl ring, confirmed the 1,4-position of acetylene group.

Polymerization of 1,4-Diethynyl-2,5-dibutoxybenzene

50 mg of *N,N,N',N'*-tetramethylethylenediamine, 50 mg of cuprous chloride, and 10 ml of pyridine were dissolved in 50 ml of chlorobenzene, and oxygen was bubbled into the solution for 30 min. 500 mg of the monomer **3** was added to the solution and was stirred for 6 h. The mixture was poured into 200 ml of methanol. The residue was washed with acetone 1 *N* hydrochloric acid, and then with methanol, and dried under reduced pressure for 1 day. 420 mg of the polymer was obtained (conversion 84%). This polymer was slightly soluble in chloroform and chlorobenzene, and soluble in *N,N'*-dimethylimidazolidinone (DMI) and 1,1,2,2-tetrachloroethane (TCE) at 150°C .



Scheme 1. Synthesis of 1,4-diethynyl-2,5-dibutoxybenzene. (a) *n*-butylbromide, triethylbenzylammonium chloride; (b) bromine; (c) trimethylsilylacetylene, CuI, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$; (d) KOH.



Scheme 2. Polymerization of poly(1,4-diethynyl-2,5-dibutoxybenzene). (e) CuCl, *N,N,N',N'*-tetramethylethylenediamine, O_2 .

Measurement

UV-VIS absorption spectrum of the polymer solution in chlorobenzene was obtained by using a Hitachi 557 double beam spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded by using a JEOL GX-270 spectrometer, respectively. DSC curve and X-ray diffraction pattern of the polymer were obtained by using a Perkin Elmer II and a Rigaku Denki Geigerflex diffractometer, respectively.

The sample film (thickness $10\ \mu\text{m}$) for measurement of current-voltage characteristics was coated on an aluminum substrate by cast of the polymer solution in DMI at 150°C , and gold was vacuum-deposited on the film as electrode. The iodine doped film was made by similar procedure from the polymer solution containing excess iodine. Current-voltage characteristics were measured by a Keithley 617 electrometer with positive voltage applied on the aluminum side under reduced pressure at room temperature. Photocurrent was measured with white light of an Ushio Denki Xe lamp (intensity $43\ \text{mW cm}^{-2}$) irradiated through the gold electrode.

RESULTS AND DISCUSSION

Polymerization and Structure of Poly(1,4-diethynyl-2,5-dibutoxybenzene (PDEDBB))

The monomer was polymerized by oxidative coupling polymerization. After the monomer was added to the catalyst solution, the temperature of the solution rose from 20°C to *ca.* 40°C . The solution color changed to yellow to green. The polymer precipitated within 3 h. The polymerization was carried out by using various amounts of catalyst, cuprous chloride. The conversion of the polymerization became less than 20% when the ratio of catalyst to the monomer was less than 5 wt%. When the ratio was more than 50 wt%, the obtained polymer was insoluble. These results indicate that there was interaction between copper ion and the generated diacetylene group.¹¹ In case of using

a small amount of catalyst, the precipitates of the polymer adsorbed most of catalyst so that the polymerization did not proceed well. In case of using large amount of catalyst, the catalyst adsorbed by the polymer caused ionic cross-linking of the polymer main chain and the polymer became insoluble. Thus, the polymer, which was obtained by using 10 wt% of catalyst, was investigated in this work to avoid the side reaction by cuprous ion.

The ^{13}C NMR spectra of the polymer and the monomer were compared in Figure 1. In spectrum of the monomer, a peak at 83 ppm is due to end carbon of acetylene group, on the other hand, the spectrum of the polymer did not have the peak. This suggests that the polymer had relatively high molecular weight. Furthermore, the spectrum of the polymer had no peak due to by-product structure such as $-\text{C}=\text{C}-$. These results indicate that the polymer had an expected structure without defects generated by side reactions.

In Figure 2, the UV-absorption spectra of the polymer and the monomer structure are compared. The absorption edge in the spectrum of the polymer, which is around 540 nm in that of the monomer, is shifted bathochromically to *ca.* 600 nm. However, the value of the red shift was less than that expected for all conjugated polymers.¹¹

To study about the conformation of the polymer main chain, solid state CP/MAS ^{13}C NMR spectrum of the polymer was measured. The ^{13}C NMR spectra are compared in Figure 3. The remarkable difference between the two spectra is that two of the aromatic carbon peaks, which are singlets in the solution spectrum, are splitted to doublets. This result implies that there are at least two kinds of phenyl group in the solid state of the polymer. There is one possible explanation as follows for these splitting of the peaks. The single bonds between two triple bonds of diacetylene groups can rotate freely and the conjugation of the polymer main chain is isolated. The result of the UV-absorption spectra supported this

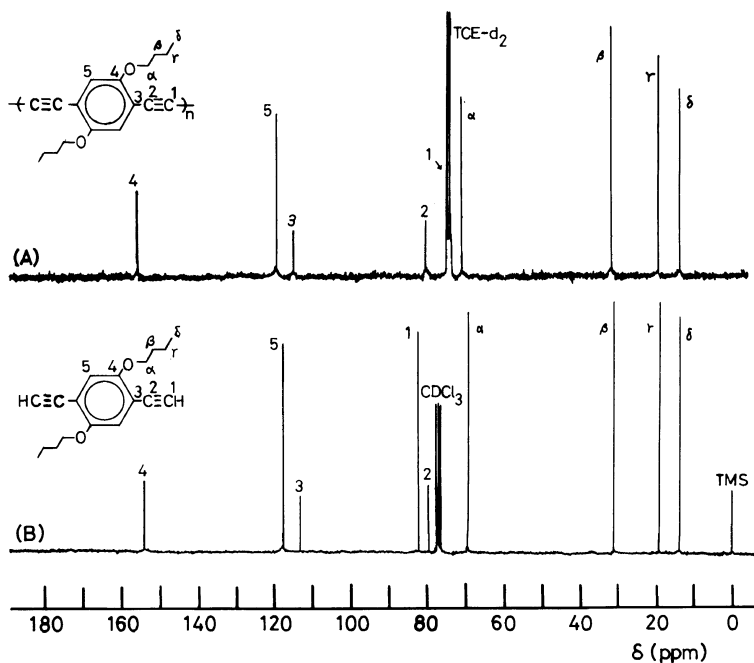


Figure 1. ^{13}C NMR spectra of poly(1,4-diethynyl-2,5-dibutoxybenzene) (A) and 1,4-diethynyl-2,5-dibutoxybenzene (B).

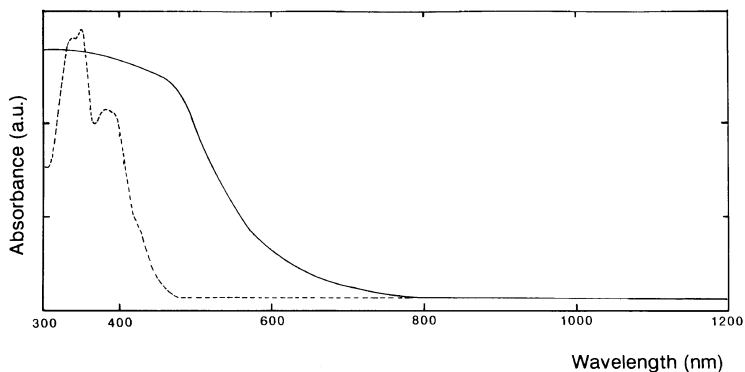


Figure 2. UV-absorption spectra of 1,4-diethynyl-2,5-dibutoxybenzene and poly(1,4-diethynyldibutoxybenzene). ---, monomer; —, polymer.

assumption. Thus, the polymer could have two kinds of conformation as shown in Figure 4. In the conformation of Figure 4(A), the neighboring two phenyl groups are conjugated and, in that of Figure 4(B), these are not conjugated.

Thermal Property of PDEDDB

The DSC curve of the polymer is shown in Figure 5. The first heating curve has a change in thermal capacity, which may be attributed to the motion of alkyl groups, and an endothermic peak at 620 K. When the polymer was not heated at 620 K, the cooling curve had the signal due to the change of thermal

Poly(1,4-diethynyl-2,5-dibutoxybenzene)

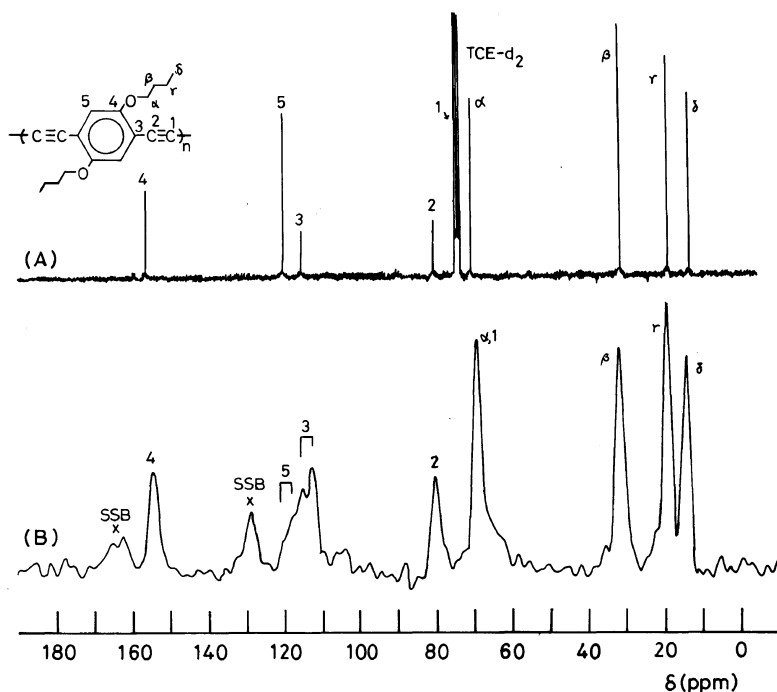


Figure 3. ^{13}C NMR spectra of poly(1,4-diethynyl-2,5-dibutoxybenzene). (A) Solution in 1,1,2,2-tetrachloroethane- d_2 ; (B) in solid state.

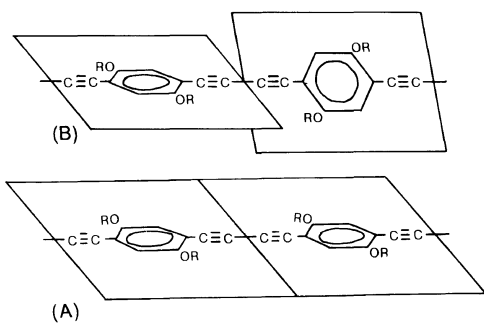


Figure 4. Proposed conformation of poly(1,4-diethynyl-2,5-dibutoxybenzene) in solid state.

capacity. This result suggests that the cross-linking reaction between diacetylenes occurred at this temperature. Generally, the reactions between them in low molecular weight compounds take place at temperatures below 620 K. Thus, at this temperature, the single bonds in main chains might begin to rotate and the cross-linking reaction might occur between diacetylene groups because steric hinderence

might be reduced.

Electrical Property of PDEDBB

The X-ray diffraction patterns of the powder of the as prepared polymer and the cast film of the polymer are shown in Figure 6. The pattern of the powder has three peaks at $2\theta = 16, 21, 25$, indicating that the polymer has crystallinity. However, the pattern of the film has no peak except halo. By using this amorphous film, the electrical properties were investigated.

The current-voltage characteristics of the polymer film is depicted in Figure 7. The dark current is 100 pA at 100 V and the conductivity was determined to 10^{-9} Scm^{-1} . This value was very low and in the range of insulators because of the isolated polymer main chain. By doping with iodine, the current became thirty times higher than the dark current. UV-VIS absorption spectrum of the iodine doped polymer film had no absorption due to charge

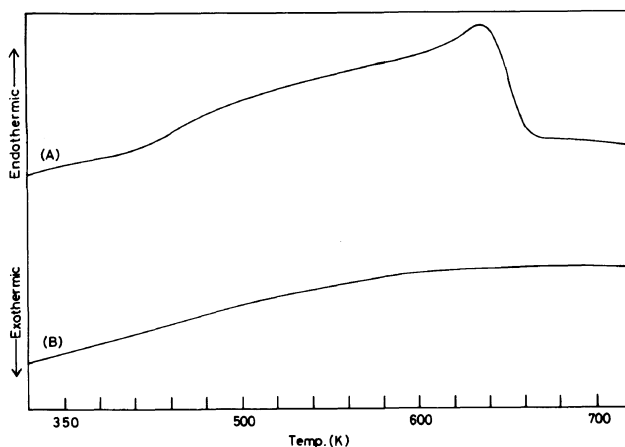


Figure 5. DSC curve of poly(1,4-diethynyl-2,5-diethynylbenzene). (A) first heating; (B) second heating; heating rate, 10 deg/min.

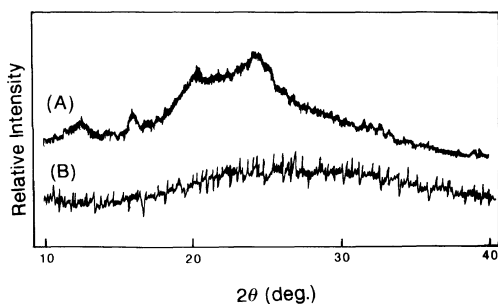


Figure 6. X-Ray diffraction pattern of poly(1,4-diethynyl-2,5-diethynylbenzene). (A) as prepared polymer powder; (B) cast film.

transfer complex between iodine and the polymer main chain although that of the dichloroethane solution of the monomer and iodine had the absorption of charge transfer complex between the monomer and iodine. So that, the increase of current is low and considered to be attributed to the iodine, and not to the complex between iodine and the polymer because the bulky alkyl groups might hinder the formation of the complex. The photocurrent became forty times higher than the dark current by irradiation with white light. This photocurrent was observed only when positive voltage was applied on aluminum side. Same photoconductive behavior was observed when a sandwich device, Al/amorphous

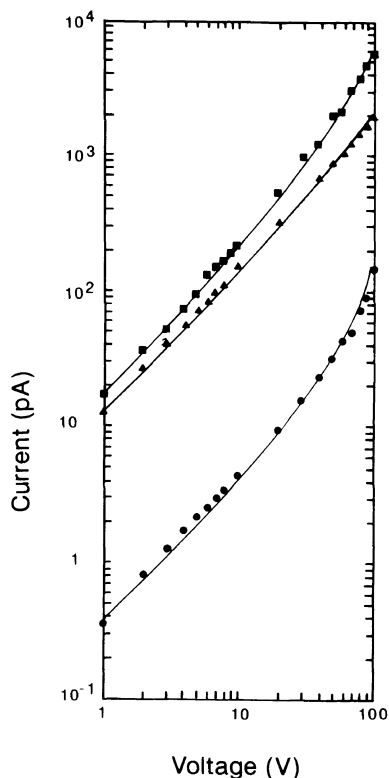


Figure 7. I-V characteristics of poly(1,4-diethynyl-2,5-diethynylbenzene). (●), dark current; (▲), I₂ doped; (■), photocurrent.

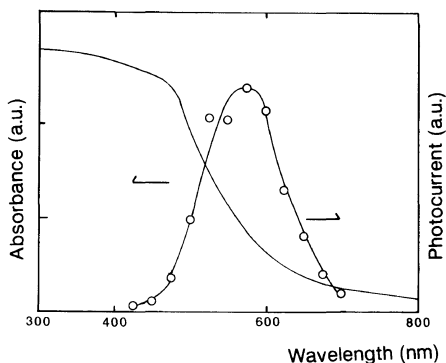


Figure 8. Wavelength dependence of photocurrent (○) in poly(1,4-diethynyl-2,5-dibutoxybenzene).

Se/PDEDDB/Au, having a Se layer for carrier generation was measured. Thus, most of the carriers are considered to be holes. Further, because the polymer had no large conjugated main chain, this photoconductivity of the polymer might be derived from the nature of the repeating unit, 1,4-dibutadiynyl-2,5-dibutoxybenzene. The action spectrum photocurrent was compared with UV-VIS absorption spectrum in Figure 8. A filter effect due to the absorption of the polymer was clearly observed when irradiated through the gold electrode, which indicates that the Schottky barrier was formed between the polymer and aluminum substrate, and the carrier (hole) was generated in the barrier.¹²

CONCLUSIONS

Poly(1,4-diethynyl-2,5-dibutoxybenzene) was soluble and had good film forming property. However, because this polymer had

bulky *n*-butoxy group, all of the neighboring phenyl groups were not conjugated by the rotation around the single bonds between triple bonds of diacetylene groups. In order to this isolated conjugated main chain of the polymer, the polymer was found to be insulator. However, the polymer exhibited relatively high photoconductivity derived from the nature of the repeating units.

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