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Synthesis and Solid-State Polymerization of Novel Diacetylenes for Nonlinear Optics

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Novel unsymmetrical diacetylenes having a carbazolyl group directly bound to acetylene moiety, i.e. 1-(N-carbazolyl)-penta-1,3-diyne-5-ol(CPDO) and the derivatives were synthesized. These diacetylenes can be topochemically polymerized in the solid state and the absorption edges of the polymers are expanded to near infrared, suggesting that π-conjugation of the main chain becomes longer by the electrons donated from carbazolyl groups. From the action spectrum of photocurrent, the band gap energy of poly-CPDO was evaluated to be 1.6 eV, which is smaller than those of so-far-known polydiacetylenes. The ionization potential was estimated to be 4.4 eV.

INTRODUCTION

Solid state polymerization of diacetylenes is known to give peculiar single crystals of conjugated polymers[1] and has attracted attention on their physical properties, such as conductivity,[2–5] optical nonlinearity[6] and mechanical strength.[7] Especially, it is interesting that the value of the third order nonlinear optical susceptibility is very large ($\chi^{(3)} = 10^{-9} \sim 10^{-10}$ esu) and the response is very fast (less than pico second order).[8–10] The susceptibility $\chi^{(3)}$ is known to be related to the band gap energy Eg by $\chi^{(3)} \propto Eg^{-6}$. Therefore, smaller Eg, that is to say more π electrons involved in conjugation, causes biger $\chi^{(3)}$. However, there must be little difference among most polydiacetylenes which have methylene groups next to diacetylene moiety and have almost the same numbers of π-electrons per repeating unit, such as poly(2,4-hexadiynediol-1,6-bis-p-toluenesulfonate) (poly-PTS),[11] poly(1,6-di(N-carbazolyl)-2,4-hexadiyne) (poly-DCHD),[12] poly(5,7-

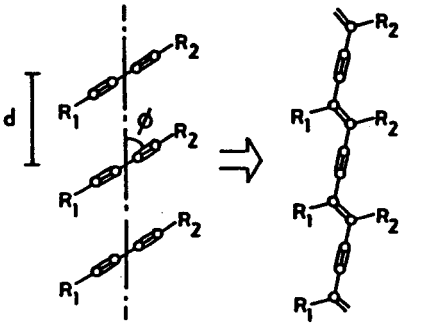


FIGURE 1 Solid state polymerization scheme of diacetylenes: $d \approx 5$Å, $\phi \approx 45°$.

dodecadiynediol-1,12-bis-phenylurethane) (poly-TCDU),[13] and so on. To achieve higher susceptibility, a polydiacetylene with π-electron rich side group directly bound to main chain and therefore, increased numbers of π-electrons per repeating unit might be a better candidate. However, few such polydiacetylenes are known: e.g. diphenyldiacetylene and dicarbazolyldiacetylene[14] are not polymerizable, and several substituted diphenyldiasetylenes give polymers only in low conversion.[15,16]

In polymerizable diacetylene crystals packing parameters, d and ϕ shown in Figure 1, are known to be near 5 Å and 45°, respectively.[17,18] Such a crystal structure is usually observed in diacetylenes which have methylene groups next to diacetylene moiety. In these crystals, bending in the methylene groups seem to produce the polymerizable stacks. So, in order to obtain the polydiacetylene with direct conjugation between polymer backbone and side groups, the synthesis of unsymmetrical diacetylenes which have both an aromatic ring and a methylene group directly bound to acetylene moieties seems to be promising as shown in Figure 2.

In this paper, we report the synthesis and the solid state polymerization of such novel diacetylenes and the optical and electrical properties of the polymers.

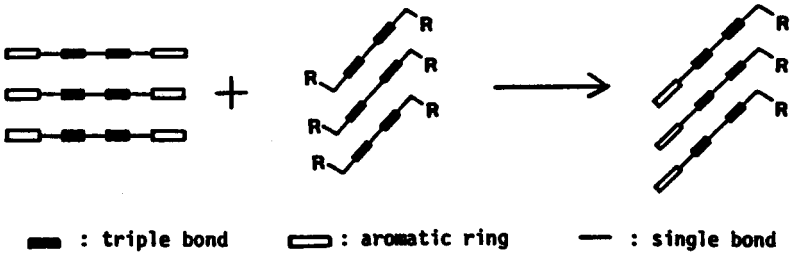
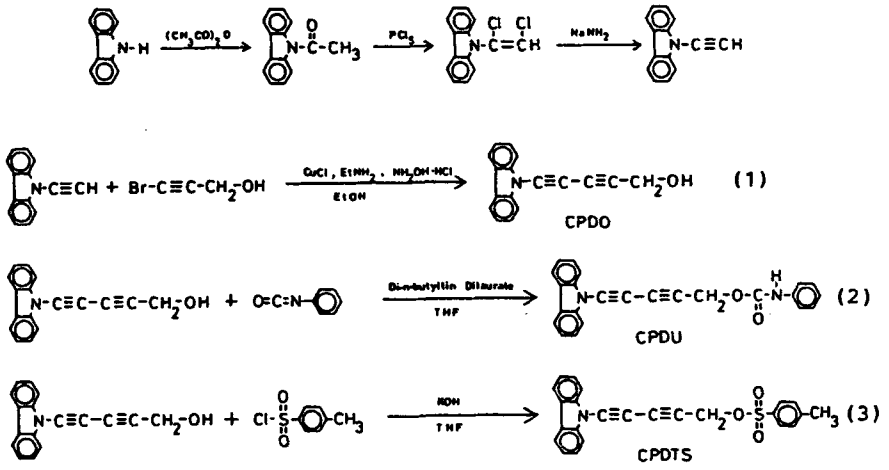


FIGURE 2 Schematic representation of molecular design of polymerizable diacetylenes with directly bound aromatic ring.

Synthesis and polymerization

1-(N-carbazolyl)*p*enta-1,3-*d*iyne-5-*o*l(CPDO) was prepared by the Chodkiewicz and Cadiot coupling[19] of N-ethynyl-carbazole[20] and 1-bromopropargyl alcohol[21] as shown by scheme (1). Catalyst solution was made from Cu(I)Cl(0.1 mmol), 70% aqueous solution of ethylamine(1 ml), and ethanol(2 ml) under an Ar atmosphere. N-Ethynylcarbazole(1 mmol) was disolved in the catalyst solution and then 1-bromoprogargyl alcohol (1.2 mmol) was added dropwise at 35°C for 2 hours. When the solution became blue due to the presence of the Cu^{2+} ion, a little $NH_2OH{\cdot}HCl$ was added for reduction of Cu^{2+} to form Cu^{1+}. The reaction mixture was evaporated and extracted with benzene. The products were isolated by column chromatography on silica gel with benzene. The yield was 21% of N-ethynylcarbazole. Two derivatives of CPDO, i.e. CPDU and CPDTS were synthesized by reactions with phenylisocyanate and p-toluenesulfonyl chloride, as shown by Scheme (2) and (3), respectively. Purification was also done by column chromatography on silica gel with chloroform. Yields were 98% and 53% of CPDO, respectively. The chemical structures of these three diacetylenes were confirmed by IR, ^{1}H-NMR spectroscopy and elemental analysis. The spectral data and melting points are listed in Table I. Two IR absorptions of triple bonds are observed because these diacetylenes are unsymmetrical.

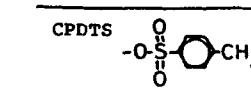
Solid-state polymerization of these diacetylenes were carried out by heating below their melting points, γ-ray irradation, or UV irra-



Scheme 1 Scheme of synthetic procedures of CPDO and the derivatives.

TABLE I

Spectral data and melting points.

	R	IR / cm^{-1}	^{1}H-NMR δ / ppm	mp / °C
CPDO	-OH	3350 (-OH) 2258,2172 (C≡C) 1450 (Cz ring)	1.75 (-OH) 4.45 (CH_2) 7.35,7.50 7.66,7.99 } (Cz)	132
CPDU		3310 (N-H) 2248,2172 (C≡C) 1700 (C=O) 1450 (Cz ring)	5.01 (CH_2) 6.72 (N-H) 7.40 (Bz) 7.35,7.51 7.66,8.00 } (Cz)	160
CPDTS		2234,2172 (C≡C) 1450 (Cz ring) 1170 (SO_2)	2.41 (CH_3) 5.78 (CH_2) 7.35,7.51 7.66,8.00 } (Cz) 7.38,7.87 (Bz)	111

Elemental analysis (%)

CPDO for $C_{17}H_{11}NO$:	calcd.	C: 83.25, H: 4.52, N: 5.71
	found	C: 83.54, H: 4.68, N: 5.66
CPDU for $C_{24}H_{16}N_2O_2$:	calcd.	C: 79.11, H: 4.44, N: 7.69
	found	C: 79.11, H: 4.43, N: 7.68
CPDTS for $C_{24}H_{11}NO_3S$:	calcd.	C: 72.16, H: 4.29, N: 3.51
	found	C: 72.07, H: 4.32, N: 3.38

dation of the crystals in vaccum vessels. ^{60}Co γ-ray with the dose rate of 1 Mrad/hr or low pressure mercury lamp (4W) was used for the polymerizations. Time conversion curves of thermal and UV polymerization were shown in Figure 3, where the conversion was determined by IR absorption intensity of triple-bond stretching vibration in comparison with that of carbazole carbon skeleton. Since two triple-bond stretching vibrations decreased in the same proportion, it is obvious that the polymerization proceeds by 1,4-addition. CPDO and CPDU reached 100% conversions by thermal polymerizations for ca. 40 hr at 80°C and ca. 20 hr at 120°C, respectively. The quantitative conversion was also confirmed by graviometry; no monomer was extracted by any organic solvents. In the case of CPDTS thermal decomposition with the elimination of sulfonyl group occured even at 50°C. By UV irradiation, the polymerization of these three diacetylenes was saturated at about 60% conversion. This is simply because the polymer formed near the cyrstal surface absorbs UV light. By γ-ray irradiation it took about 600 hrs to reach 100% conversion in all cases.

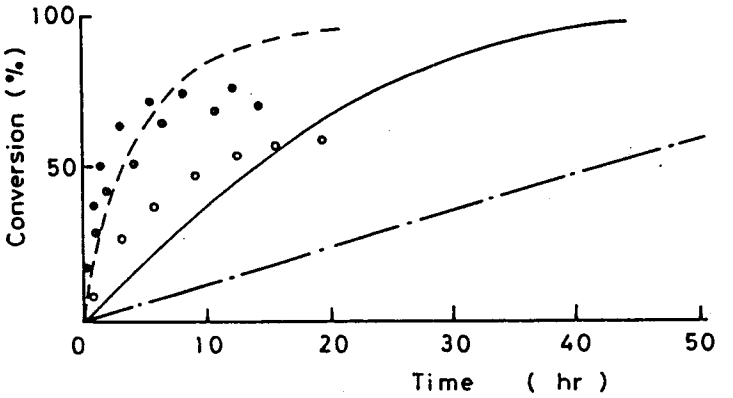


FIGURE 3 Time-conversion curves of the thermal and UV polymerization. ————(80°C) CPDO, —.— (80°C), ———— (120°C) CPDU. UV irradiation: ○; CPDO, ◑; CPDU, ●; CPDTS.

Since among these diacetylenes only CPDO could be grown to big crystals, x-ray crystallographic study was carried out with CPDO and poly-CPDO. Cell parameters and full intensity data for crystal structure analysis were obtained at room temperature on a 4-circle diffractometer, using a $2\theta/\omega$ scanning routine and graphite-monochromatized Cu-Kα radiation (λ = 1.54178Å). Their crystal data was shown in Table II. As shown in Figure 4, the molecules are stacked with a repeating distance of 4.951 Å and the inclination angle of 46.11° to the b-axis. These parameters are well in the range of highly polymerizable packing. As expected, the bending in a methylene group plays an important role in causing polymerizable stacks. Since the space group of the polymer is the same as that of the monomer,

TABLE II

Crystallographic data of CPDO and poly-CPDO.

	Monomer	Polymer
Formular	$C_{17}H_{11}NO$	$C_{17}H_{11}NO$
Mr	245.3	245.3
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/a$	$P2_1/a$
a (Å)	16.249(3)	16.494(6)
b (Å)	4.951(1)	4.873(3)
c (Å)	17.360(4)	19.513(8)
β (°)	113.53(2)	124.27(3)
V (A^3)	1280.4(5)	1296 (1)
Z	4	4
Dx(Mg m^{-3})	1.27_3	1.25_6
Dm(Mg m^{-3})	1.27	1.26

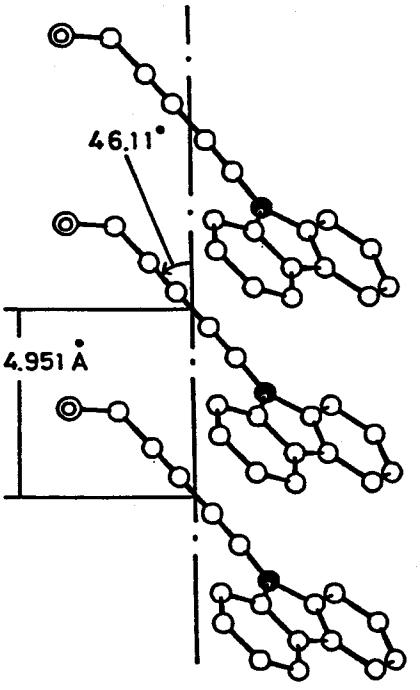


FIGURE 4 Molecular arrangement of CPDO along the b-axis; ○: C; ◎: 0, ●: N.

this polymerization can be concluded to be typical topochemical reaction. However, the crystal structure of the polymer could not be analyzed because x-ray diffractions were so diffused and only small numbers of intensity data were available.

Optical and electrical properties

The samples for optical measurements were prepared by spraying chloroform solutions of monomers on glass plates and evaporating the solvent. The film thickness was submicron order. These diacetylenes do not absorb visible light, though the thin films looked white because of the rough surface. Absorption spectra after 60 min of UV irradation are shown in Figure 5. The absorption maxima of CPDO, CPDU, and CPDTS are at 670, 610, and 430 nm. Their colors were green, blue purple, and brown, respectively. By further irradiation, their colors became darkened and the absorption edges were expanded to near infrared, as is representatively shown by poly-CPDO in Figure 6. Since the spectra of poly-CPDU and poly-CPDTS became

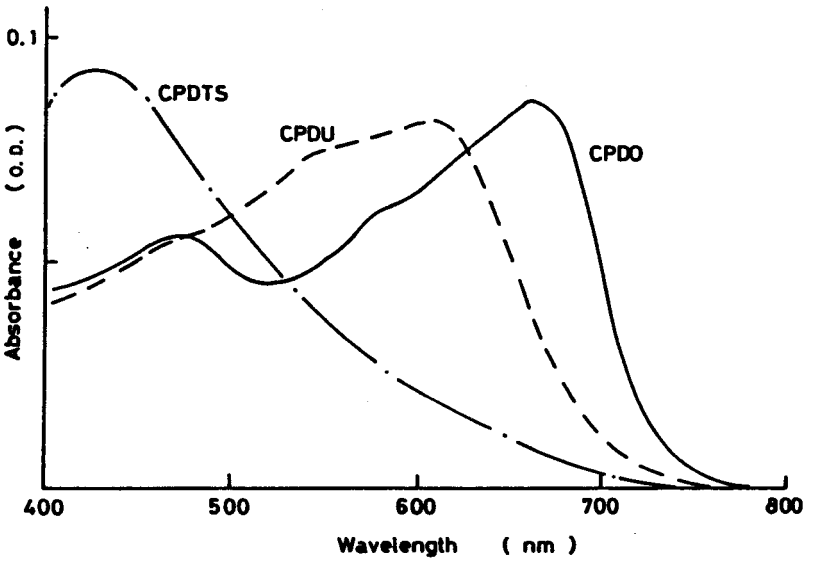


FIGURE 5 Absorption spectra of CPDO, CPDU, and CPDTS after UV irradiation for 60 min.

ambiguous, i.e. no peaks and monotonous, and they did not give big crystals, following investigations were carried out with only poly-CPDO.

The photocurrent of poly-CPDO was measured by setting two gold electrodes with a 0.5 mm gap and 1 mm width on the polymer single crystal surface along the main chain. At applied voltage of 500 V, the dark current was 1×10^{-11} A and the photocurrent was 2×10^{-11} A upon the illumination of 450 nm with 0.1 mW/cm^2. Measured by the same manner, the dark and photocurrent of poly-DCHD was 5×10^{-13} and 2×10^{-11} A, respectively. The dark conductivity of poly-CPDO is two orders of magnitude bigger than that of poly-DCHD. This must be the reason why the current increment of poly-CPDO upon photo-illumination is apparently smaller. For the measurement of action spectra, a 150 W xenon arc lamp and a grating monochromator were used and the photocurrent was normarized in relative value corresponded to the light power of 10^{14} photons. As seen in Figure 6, the action spectrum and the absorption spectrum coincide with each other. Thin film of the polymer crystallites made on a glass plate also gave the same action spectrum. Semiconductor theory[22] predicts that photocurrent i and absorption coefficient α are related to photon energy $\hbar\omega$ by $(i\alpha\hbar\omega)^{0.5} \simeq (\hbar\omega\text{-Eg})$. So, the band

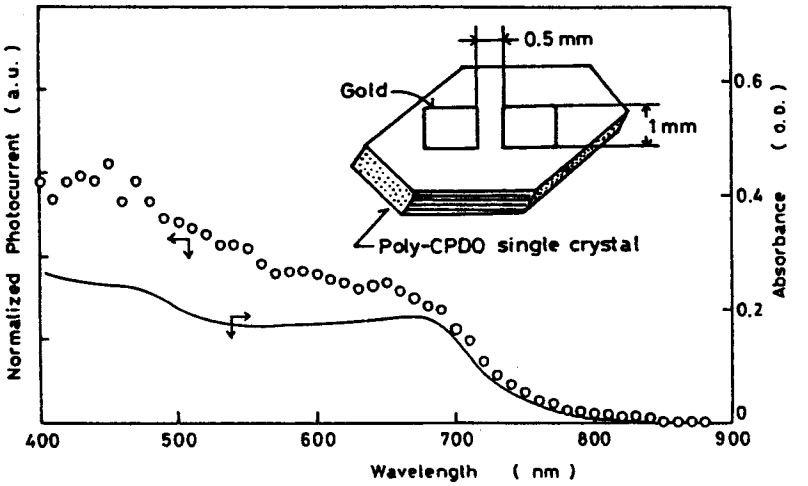


FIGURE 6 Action spectrum of photocurrent (○) and absorption spectrum (——) of poly-CPDO.

gap energy of poly-CPDO was evaluated to be 1.6 eV by extrapolating the linear part of $(i\alpha\hbar\omega)^{0.5}$ vs. $\hbar\omega$ plot (○) in Figure 7, where optical density was used instead of absorption coefficient.

When a Al/poly-CPDO/NESA sandwich cell was made, a rectification behavior was recognized as shown in Figure 8, in which the

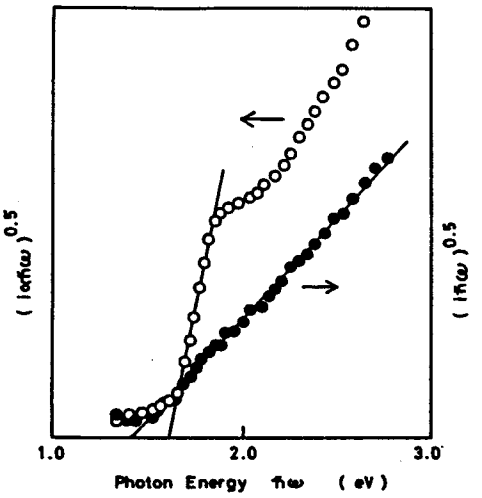


FIGURE 7 Plots according to semiconductor theory; ○: $(i\alpha\hbar\omega)^{0.5}$ vs. photon energy for surface cell of poly-CPDO, ●:$(i\hbar\omega)^{0.5}$ vs. photon energy for Al/poly-CPDO/NESA at −2V applied to Aluminum electrode.

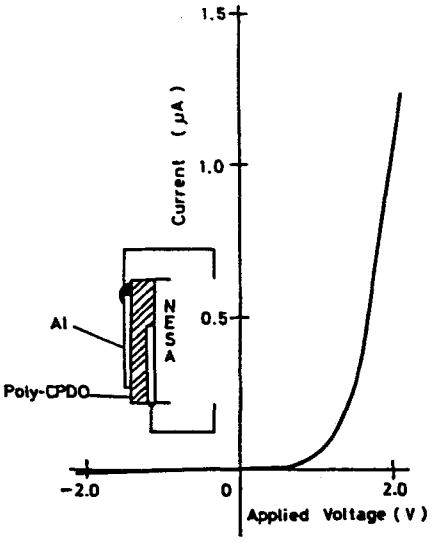


FIGURE 8 Dark I-V curve of Al/poly-CPDO/NESA sandwich cell. The sign of the potential is that applied to Al.

forward bias potential corresponds to the aluminum electrode being positive. However, photovoltaic effect was not observed. The barrier height for electron moving from aluminum electrode to poly-CPDO was evaluated to be 1.4 eV by the plot of photocurrent vs. photon energy in Figure 7 (●). Since the work function ϕ_m of aluminum (4.2 eV) is relatively small,[23] aluminum usually makes Schottky barrier on a p-type organic semiconductor.[24,25] In that case the forward bias potential is negative to aluminum electrode. However, the rectification behavior in Figure 8 is just the reverse of usual cases; it can be understood by an assumption that poly-CPDO is an intrinsic semiconductor. Band energy relation between aluminum and poly-CPDO is schematically shown in Figure 9. By the above assumption, the fermi level ϕ_s of poly-CPDO can be laid at the center of the band gap. Since the barrier height from aluminum electrode to poly-CPDO corresponds to the difference between the electron affinity χ_s and the work function ϕ_m, the χ_s is evaluated to be 2.8 eV and therefore the ionization potential Ip, which is the sum of χ_s and Eg, becomes 4.4 eV. The fermi level ϕ_s is estimated to be 3.6 eV and is 0.6 ev higher than ϕ_m of aluminum. However, Schottky barrier as shown in Figure 9 (b) is not formed, because the amount of charge carrier in poly-CPDO is very small and therefore a flow of charge carrier from poly-CPDO to aluminum electrode does not occur to attain the equilibrium

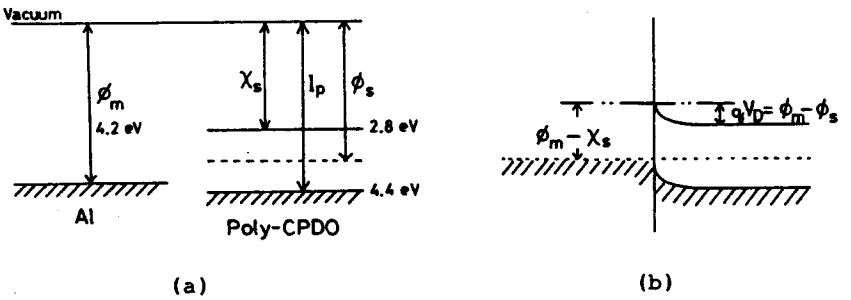


FIGURE 9 Schematic representation of band energy relation between aluminum and poly-CPDO.

of fermi level. So, the band energy relation in Figure 9 (a) seems to remain after their contact. Even in the absence of Schottky barrier, a barrier of $\chi_s - \phi_m$ contributes to the rectification behavior. $\phi_s - \phi_m$ of -0.6 eV well agrees with the value of -0.6 V at the crossing point of the I-V curve in Figure 8.

According to the above mentioned result, the band gap energy and ionization potential of poly-CPDO are 1.6 and 4.4 eV, respectively. This band gap energy is smaller than those of other polydiacetylenes; e.g. 2.1 eV for poly-PTS 2.3 eV for poly-DCHD.[22] This is a clear indication of that the π-conjugation of poly-CPDO becomes longer by the electron donating group directly bound to the main chain.

CONCLUSION

By the molecular design of polymerizable diacetylene in solid state, polydiacetylenes with carbazolyl group directly bound to the main chain have been synthesized. Since the band gap of 1.6 eV is smaller than that of poly-PTS with extraordinarily large $\chi^{(3)}$, the nonlinear optical properties are expected to be far larger.

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