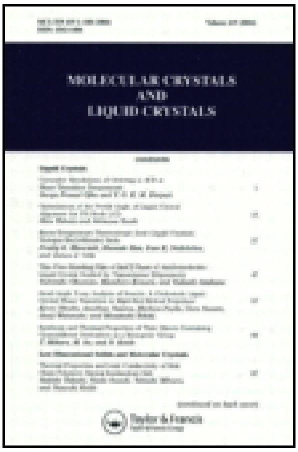

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Tadahiro Shibuya [a], Yoko Tatewaki [a] & Shuji Okada [a]
[a] Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Japan

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Synthesis of Polydiacetylenes with Pyridyl Groups Directly Bound to the Main Chain

TADAHIRO SHIBUYA, YOKO TATEWAKI,
AND SHUJI OKADA*

Graduate School of Science and Engineering, Yamagata University, 4-3-16
Jonan, Yonezawa Japan

N-Substituted carbamic acid esters of 8-pyridyl-5,7-octadiyn-1-ol were synthesized and all the monomers showed solid-state polymerizabilities by UV irradiation to give polydiacetylenes with pyridyl groups directly bound to the π-conjugated backbone. Hydrogen-bond complexes of these monomers with dodecanoic acid (DA) or perfluorododecanoic acid (PFDA), in which the pyridyl nitrogen atom formed a hydrogen bond with the hydrogen atom of the carboxyl group, were also prepared. Although complex formability of DA with the monomers in this study was not so high, many PFDA complexes were obtained because of the higher acidity. All complexes could be polymerized in the solid state and the conversion increased by complexation compared with the original monomers. More favorable monomer stacking for solid-state polymerization could be achieved by combination of intermolecular hydrogen bonds between urethane groups and alkyl (or perfluoroalkyl) chain packing.

Keywords Solid-state polymerization; conjugated polymer; polydiacetylene; pyridyl group; hydrogen-bond complex

1. Introduction

Polydiacetylenes (PDAs) can be obtained by solid-state polymerization of butadiyne monomers as π-conjugated polymer single crystals [1]. Since third-order nonlinear optical susceptibilities of PDAs have been reported in 1969 for the first time among the conjugated polymers [2], a lot of researches on PDAs as third-order nonlinear optical materials have been performed. We have been studying about extension of the π-conjugated structure of PDA for improved optical and electronic properties. One of the strategies is introduction of conjugated side groups such as aromatic rings [3–5]. Among the aromatic groups, pyridyl groups have some interesting properties, i.e., hydrogen-bond formability by acting as a proton acceptor, salt formability by reacting with acid, and metal-complex formability. These characteristics may be used for adjustment of monomer arrangement in crystals and changes in electronic structures of π-conjugation systems. In our previous communication, we prepared 4-pyridylbutadiyne derivatives with a urethane group and their conversions were generally improved by complexation with dodecanoic acid (DA) [6]. In this study, we extended the system into 2-pyridyl and 3-pyridyl derivatives. These monomers and their

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[*] Address correspondence to Shuji Okada, Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan. E-mail: okadas@yz.yamagata-u.ac.jp

hydrogen-bond complexes with DA or perfluorododecanoic acid (PFDA) were prepared and their solid-state polymerization behaviors were compared.

2. Experimental

Pyridylbutadiyne derivatives **2a–2f**, **3a–3f** and **4f** were synthesized according to Fig. 1. Compound's numbers **2**, **3** and **4** indicate 2-pyridyl, 3-pyridyl and 4-pyridyl derivatives, respectively, and **f** is for bifunctional monomers. A urethane group was introduced to align monomers in a polymerizable stack by the intermolecular hydrogen bonding between adjacent monomers. Their chemical structures were confirmed by ^{1}H- and ^{13}C-NMR spectra, IR spectra and elemental analyses. Melting points of the monomers measured by a SII DSC 220 differential scanning calorimeter are included in Table 1. For preparation of the hydrogen-bond complexes of **2a–2e** and **3a–3e** with DA or PFDA, equimolar solutions of a pyridyl butadiyne and DA or PFDA were mixed and solvent was evaporated. For **2f**, **3f** and **4f**, two equivalents of DA or PFDA were mixed. Solvent used were ethyl acetate for DA and chloroform-ethyl acetate mixture for PFDA. Solid-state polymerization was confirmed by irradiating UV light at 254 nm from a 4-W lamp (UVP, UVG-11). Conversion of monomers to the corresponding polymers was calculated from decrease in IR peak intensity corresponding to $\nu_{C\equiv C}$ or from heat of melt of the monomer remaining in the polymerized sample. UV-visible diffuse reflectance spectra were measured using a Jasco V-570 spectrophotometer with an integrated sphere (ILN-472). Powder X-ray diffraction patterns were recorded on Rigaku RINT-Ultimate III and Ultimate IV diffractometers.

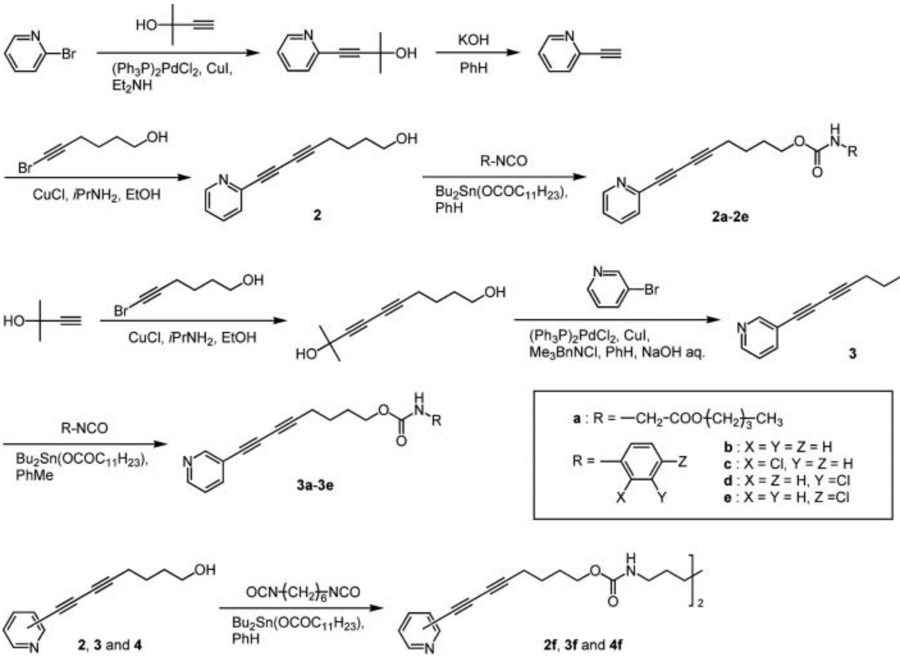

Figure 1. Synthesis scheme of pyridylbutadiyne derivatives in this study. 2-Pyridyl, 3-pyridyl and 4-pyridyl derivatives are indicated by compound's numbers **2**, **3** and **4**, respectively.

Table 1. Melting point of monomers, polymer excitonic absorption wavelength (λ_{ex}), polymer absorption cutoff wavelength (λ_{ex}) and conversion (c) by UV irradiation of monomers and complexes

	Original monomer				DA complex			PFDA complex		
	Mp/°C	λ_{ex}/nm	λ_{co}/nm	c/%	λ_{ex}/nm	λ_{co}/nm	c/%	λ_{ex}/nm	λ_{co}/nm	c/%
2a	53	$-^{a}$	800	17^{b}			NC^{d}	625	785	40^{b}
2b	85	$-^{a}$	695	10^{b}			NC^{d}	$-^{a}$	670	28^{b}
2c	43	$-^{a}$	710	22^{b}			NC^{d}	$-^{a}$	770	33^{b}
2d	68	$-^{a}$	610	8^{b}			NC^{d}			NC^{d}
2e	134	$-^{a}$	550	15^{b}			NC^{d}			NC^{d}
2f	123	610	800	76^{c}			NC^{d}	$-^{a}$	800	87^{c}
3a	70	585	620	12^{b}			NC^{d}	575	690	30^{b}
3b	112	570	650	26^{b}			NC^{d}	$-^{a}$	560	32^{b}
3c	83	$-^{a}$	550	8^{b}	610	650	31^{b}	$-^{a}$	550	48^{b}
3d	100	$-^{a}$	610	7^{b}			NC^{d}	$-^{a}$	570	41^{b}
3e	149	$-^{a}$	620	12^{b}			NC^{d}	$-^{a}$	580	15^{b}
3f	123	608	750	34^{c}	612	720	87^{c}	$-^{a}$	710	81^{c}
4f	120	575	800	40^{c}	610	795	81^{c}	$-^{a}$	770	58^{c}

[a] Absorption maximum was not observed although the absorbance in the visible region increased.

[b] Conversion was calculated from decrease in IR peak intensity corresponding to $\nu_{C\equiv C}$.

[c] Conversion was calculated from heat of melt of the monomer remaining in the polymerized sample since the no peak corresponding to $\nu_{C\equiv C}$ was observed.

[d] NC means no complexation and conversion was not obtained.

3. Results and discussion

When we monitored the UV-visible spectral change depending on time of UV irradiation to the monomers, all the monomers synthesized showed absorption increase in visible region suggesting formation of π-conjugated backbones. Especially, **3a** and **3b** showed excitonic absorption bands. Monomers **2f**, **3f**, and **4f** with two pyridylbutadiynyl groups at both ends also showed clear excitonic absorption bands at longer wavelengths compared with the monomers with one pyridylbutadiynyl group. For the bifunctional derivatives, increase in hydrogen-bond number within a monomer may assist to form more appropriate alignment of monomers for the solid-state polymerization. Other monomers without showing excitonic absorption peaks seemed to have less regular structures. The cutoff wavelengths of absorption bands, the peak wavelengths of the excitonic band, and the conversions of the original monomers are summarized in Table 1 together with those of the complexes with DA or PFDA (see below).

By mixing pyridylbutadiyne derivatives with DA or PFDA, hydrogen-bond complex formation was investigated. Complexation was confirmed by the following three points. First, the IR spectrum of the mixture was not mere summation of the spectra of the two components especially in the case of DA. The peak at around 920 cm^{-1} of DA originated from O–H out-of-plane bending vibration of dimerized carboxyl groups was weakened by hydrogen-bond complex formation of DA with pyridylbutadiyne derivatives although such clear changes were hardly observed in the case of PFDA. Second, the melting point of the mixture was different from that of the original two components. Third, the X-ray diffraction patterns of the mixture were not summation of the patterns of the original two components. When the monomers were mixed with DA, production of the hydrogen-bond complexes was only confirmed for few compounds, i.e., **3c**, **3f** and **4f**. However, when more acidic PFDA was used, all monomers except **2d** and **2e** could form the hydrogen-bond complexes. When a conjugated substituent such as vinyl or phenyl group is attached to pyridine, p*K*a order of the corresponding conjugate acids is 4-pyridyl > 3-pyridyl > 2-pyridyl [7]. Even in the case of butadiynyl-substututed pyridines **2–4**, similar tendency is expected, and order of basicity is considered to be **4** > **3** > **2**. Accordingly, order of hydrogen-bond-complex formability should be 4-pyridyl > 3-pyridyl > 2-pyridyl. Actually, DA complex formation of the corresponding 4-pyridyl derivatives has been found for **4a**, **4b**, **4c** and **4e** [6], in which alphabets indicate the substituents in Figure 1, and 4-pyridyl derivatives gave five DA complexes including **4f** in this study. In Table 1, 3-pyridyl and 2-pyridyl derivatives gave two and no DA complexes, respectively. More PFDA hydrogen-bond complexes were obtained for 3-pyridyl derivatives than 2-pyridyl derivatives.

Figure 2 displays the results obtained for **3c** as an example. In UV-visible diffuse reflectance spectra after UV irradiation shown in Figure 2(a), the cutoff wavelength of the DA complex of **3c** (**3c**-DA) shifts to the longer wavelength (~650 nm) compared with that of **3c** (~550 nm). It is interesting that **3c**-DA showed weak excitonic absorption bands at around 610 nm although there were no excitonic bands for **3c**. In the case of **3f** and **4f**, excitonic bands were also retained in the corresponding DA complexes. The PFDA complex

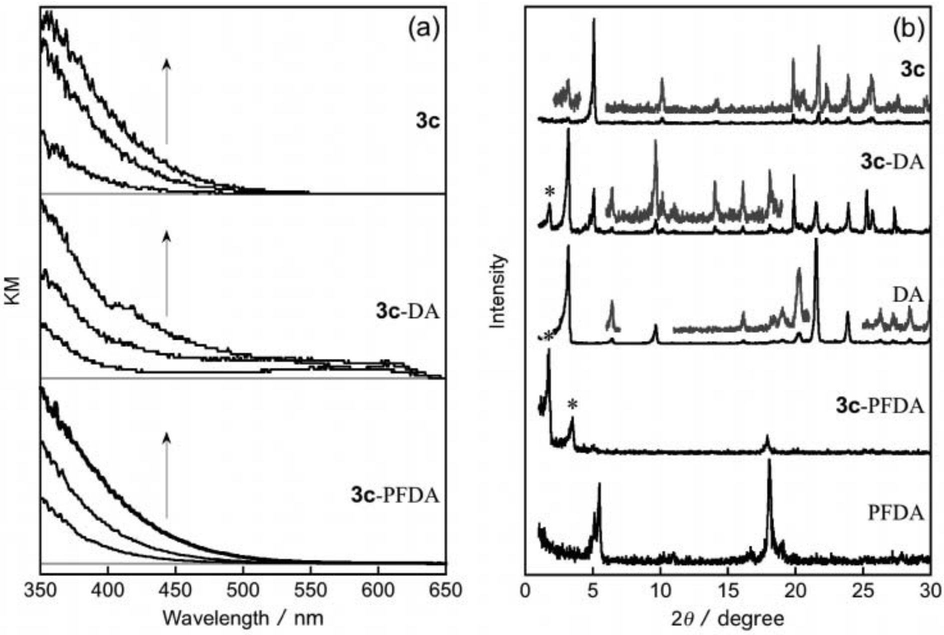

Figure 2. (a) Change in UV-visible diffuse reflectance spectra of **3c**, **3c**-DA and **3c**-PFDA during UV irradiation. For **3c** and **3c**-PFDA, UV-irradiation spans for the lower, middle and upper curves were 10 min, 1 h and 4 h, respectively, while those were 1 min, 5 min and 1 h, respectively, for **3c**-DA. (b) Powder X-ray diffraction patterns of **3c**, **3c**-DA, DA, **3c**-PFDA and PFDA. Magnified diffractograms are inserted for **3c**, **3c**-DA and DA. Asterisks indicate obviously new peaks appeared by complexation.

of **3c** (**3c**-PFDA) showed a cutoff wavelength similar to **3c**. Among PFDA complexes, only **2a**-PFDA and **3a**-PFDA showed excitonic absorption bands, and other complexes showed only absorption increase in visible region without maximum. Composition of the hydrogen-bond complexes were confirmed by measuring the powder X-ray diffractograms, and those of **3c** are shown in Figure 2(b). When the diffraction patters of **3c**-DA were compared with those of **3c** and DA, many peaks observed for **3c**-DA coincided with those of **3c** and DA suggesting that the complexation partly occurred. Partial complexation with DA was also found in **3f** while no diffraction peaks of the original compounds were observed for **4f**-DA. For the PFDA complexes, all of them showed new diffraction peaks without peaks assigned to the original pyridylbutadiyne compounds and PFDA, i.e., the complexes were obtained in quantitative yield. In the complexes irrespective of DA or PFDA, the conversions from a monomer to the corresponding PDA increased. Namely, by forming hydrogen-bond complexes with long-chain carboxylic acid, alignment of the pyridylbutadiyne derivatives was tuned to more favorable one for the solid-state polymerization.

In conclusion, original monomers synthesized could be all solid-state polymerizable because the introduced urethane group formed intermolecular hydrogen bonds to align monomers in a polymerizable stack. Dipyridyl derivatives **2f**, **3f** and **4f** showed relatively higher conversion and clear excitonic absorption, and two arrays of intermolecular hydrogen bonds seemed to be more effective to form a polymerizable stack. Complex formability of PFDA with the pyridyl monomers in this study was higher than that of DA. More acidic PFDA is apt to form hydrogen-bond complexes. All complexes could be polymerized and the conversion increased by complexation. Both intermolecular hydrogen bonds between urethane groups and alkyl (or perfluoroalkyl) chain packing resulted in more favorable stacking for the solid-state polymerization.

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