Chemistry Letters Vol.35, No.4 (2006)

Synthesis of Pyridylbutadiyne Derivatives and Improvement of Their Solid-state Polymerizability by Complexation with Alkanoic Acid

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4-Pyridyl-substituted polydiacetylenes, which have potential to form intermolecular complexes with a variety of species, were synthesized from 8-(4-pyridyl)oct-5,7-diynyl carbamate (PODC) derivatives for the first time. The monomer conversion of solid-state polymerization was improved by complexation with dodecanoic acid.

Polydiacetylene (PDA) is a unique π-conjugated polymer synthesized by topochemical solid-state polymerization.[1] Due to its excitonic absorption along the π-conjugated backbones, PDA is considered to be one of the promising third-order nonlinear optical materials.[2] In order to improve its optical properties, we have synthesized PDA derivatives with electronic intramolecular interactions, e.g., π-conjugation between polymer backbones and substituents such as aromatic rings[3] and acetylenic groups.[4] On the other hand, PDA derivatives, whose π-conjugated backbones are perturbed by electronic intermolecular interactions, have been less studied. In this regard, a pyridyl group is an interesting substituent to attach to the PDA backbones because this group is known to form salts, metal complexes, and supramolecular assembles with a carboxyl group by hydrogen bonding.[5] These intermolecular interactions must be transmitted to the π-conjugated backbone through the π-conjugated pyridyl group. Although many 4-pyridyl butadiyne derivatives have been prepared as metal ligands,[6,7] 4-pyridylbutadiyne derivatives with solid-state polymerizability have been less studied[8] and their regular 1,4-addition polymerization in solid state has not been reported so far. For topochemical polymerization of butadiyne monomers, the following molecular alignment in crystals is required: The translation distance between adjacent molecules is ca. 5 Å and the angle between translation direction and butadiyne rods is ca. 45°.[9] These conditions can be achieved by attaching specific groups to the substituents of the butadiyne monomers.[3,10]

In this study, in order to realize such conditions, we synthesized 8-(4-pyridyl)oct-5,7-diynyl carbamate (PODC) derivatives, i.e., **4a** through **4e** in Figure 1, as model compounds. Introduction of a urethane group in the linear substituent of PODC helps to align monomers into polymerizable stack. Moreover, by using the characteristic of the pyridyl group to form hydrogen bonding, we combined PODCs with simple long-chain carboxylic acid, i.e., dodecanoic acid (DDA), and improvement of conversion to polymer was investigated.

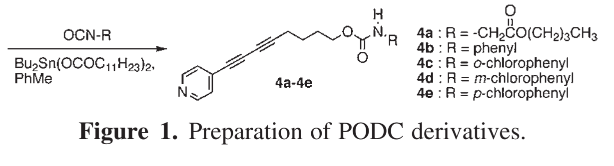

Figure 1. Preparation of PODC derivatives.

PODC derivatives **4a** through **4e** were synthesized according to the scheme in Figure 1. Compounds **1**[6] and **2**[11] were prepared according to the literatures, and these compounds were coupled by the Cadiot–Chodkiewicz reaction to give **3**. Alcohol **3** was reacted with isocyanates to give the corresponding urethane derivatives **4a** through **4e**. Equimolar ethyl acetate solutions of these compounds and DDA were mixed together. After solvent evaporation of the mixtures, residual materials, i.e., **4*x***-DDA where ***x*** is ***a*** through ***e***, were obtained.

Figure 2 shows FT-IR spectra of **4a** (a), **4a**-DDA (b), and DDA (c). Spectrum (b) is not the mere average of spectra (a) and (c). In spectrum (a), two peaks at 1737 and 1722 cm^{-1} assigned to C=O stretching vibration of ester and urethane groups, respectively, of **4a**. In spectrum (b), these peaks were shifted to lower wavenumbers at 1712 and 1693 cm^{-1} due to change in hydrogen-bonding conditions between N–H of urethane group and carbonyl groups of **4a** by combining with DDA. In addition, the peak at 920 cm^{-1} of DDA corresponding to O–H out-of-plane bending vibration of dimerized carboxyl groups in spectrum (c) disappeared in spectrum (b), and the peak at 1763 cm^{-1} in spectrum (b) is assignable to C=O stretching vibration of carboxylic acid, which makes hydrogen bonding with the pyridine moiety of **4a**. These spectral changes revealed that, in the equimolar mixture of **4a** and DDA, dimerized DDA molecules were separated and a DDA molecule was combined with a **4a** molecule. Similar FT-IR spectral changes were also observed for **4b**, **4c**, and **4e**. However, **4d** did not show such spectral changes.

Structural changes of PODCs by DDA complexation were further confirmed by measurements of melting points and pow-

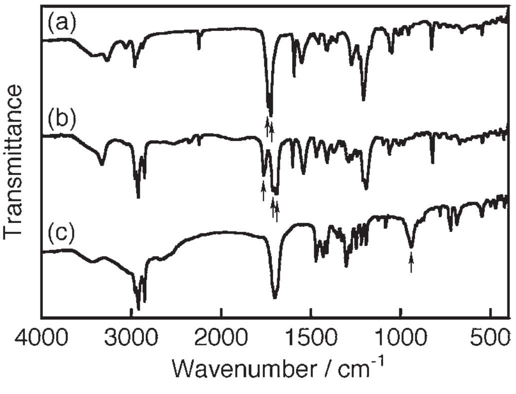

Figure 2. FT-IR spectra of (a) **4a**, (b) **4a**-DDA, and (c) DDA. Arrows indicate the peaks discussed in the text.

Table 1. Melting points, long spacings (*d*), and conversions (*c*) of DDA-combined compounds of **4a** through **4e** and their original compounds

Compound	mp/°C	*d*/nm	*c*/%
4a-DDA	41–50	3.88	79
4b-DDA	75–84	3.62	66
4c-DDA	55–66	2.00	41
4d-DDA	42–53, 91–113	1.15, 2.73	—
4e-DDA	78–86	3.71	42
4a	36–40	2.42	28
4b	85–87	3.06	9
4c	73–75	2.65	44
4d	132–134	1.15	7
4e	128–129	2.28	11
DDA	44–46	2.73	—

der X-ray diffraction patterns. Table 1 summarizes the melting points, long spacings (*d*) and monomer conversions to the corresponding polymer by UV irradiation of DDA-combined PODCs, original PODCs and DDA. Melting points were measured by DTA curves and a temperature range between two intersection points of the base line and peak slopes are shown as melting point ranges in Table 1. All the DDA-combined PODCs except **4d** showed unique melting points although the melting ranges were broad compared with the original compounds. They showed diffraction patterns different from those of the original compounds. The *d* spacing values of DDA-combined PODCs are explained by the bilayer structure for **4a**, **4b**, and **4e** and the monolayer structure for **4c**. On the other hand, **4d** did not form the complex with DDA under the present experimental conditions, and it is consistent with the result of the FT-IR spectra. This reason is not clear but meta-substitution of the phenyl urethane group may be sterically disfavored to form layered structures of **4d** combined with DDA. We noticed that the *d* spacing values of original PODCs are interpreted by the bilayer structure for **4a**, **4b**, **4c**, and **4e**, while that for **4d** by monolayer structure, implying that this monolayer structure may be quite stable by sterical reason.

Photopolymerization was performed by using a 4-W UV lamp at 254 nm for KBr-pellettized samples of the PODC compounds. By UV irradiation, all the monomers and their complexes with DDA exhibited absorption increase in wavelengths longer than about 600 to 800 nm depending on the compounds (see Figure 3 as an example). At the same time, intensity of the C≡C stretching vibration peaks in the FT-IR spectra decreased. These results clearly indicate that solid-state polymerization proceeded to form π-conjugated backbones. Thus, monomer conversions were calculated by decreasing ratio of the C≡C stretching vibration peaks in the FT-IR spectra. It is interesting that conversions of most of PODCs increased when combined with DDA. This indicates that complexation with DDA helps to align PODC molecules into more polymerizable stacks. In a previous study, we had confirmed that long-chain alkyl groups assist to give the polymerizable stacks by packing effect of alkyl group,[12] and combination of DDA to PODCs was considered to show the same effect. However, in the present case, DDA is not covalently bonded to PODCs and DDA was easily removed from the polymer by washing with organic solvent. This fact is advantageous for applications for electronics and photonics because long-chain alkyl groups are inactive portions for electronic and/or optical functionalities, and their removal increases the performance.

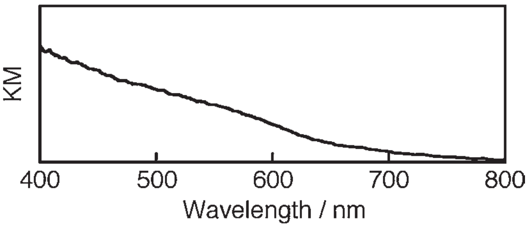

Figure 3. Diffuse reflectance spectrum of **4a**-DDA polymer.

In conclusion, we synthesized PODCs and succeeded in their solid-state polymerization to give 4-pyridyl-substituted PDAs. Their conversion was able to increase by complexed with DDA. Since polyPODCs have potential to form intermolecular complexes with a variety of species, it is worth studying about the relationship between complexation and the resulting electronic properties of the perturbed π-conjugation system in future works.

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Published on the web (Advance View) March 18, 2006; DOI 10.1246/cl.2006.412