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Structural relaxation accompanied by photo-induced chromatic phase transition of polydiacetylenes with butylene-*N*-difluorophenyl carbamate side chains

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ABSTRACT

We have studied the phase transition of poly-5,7-dodecadiyne-1,12-diol bis[2,4-difluorophenyl carbamate] (PDA-2,4-DFPC) and poly-5,7-dodecadiyne-1,12-diol bis[3,4-difluorophenyl carbamate] (PDA-3,4-DFPC) by visible reflection spectroscopy and mid-infrared absorption spectroscopy. Both PDA-2,4-DFPC and PDA-3,4-DFPC show the reflection spectra characterized by a sharp peak at around 1.9 eV at room temperature. While PDA-3,4-DFPC shows thermochromic phase transition to the phase showing the reflection spectrum with a peak around 2.2 eV above 120 °C, PDA-2,4-DFPC shows no abrupt change of the reflection spectrum. However, PDA-2,4-DFPC shows drastic change of the reflection spectrum under 532-nm CW-laser excitation. Based on these results, we can draw the following two conclusions. First, the phase transition behavior of PDA can be controlled by modifying the side-chain structure. Second, we demonstrate that thermally inaccessible phase of PDA is induced by the photo-excitation. By measuring mid-infrared absorption of PDAs, we elucidated that conformational change of side chains is accompanied with the phase transition. Based on the results, we discussed the role of the side chain in the phase transition.

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1. Introduction

The side chain of conjugated polymers has been believed to be inconsequential to the polymer properties, because many interesting features of the conjugated polymer are dominated by the nature of π -electron system extending along the main chain. However, the side chains are linked to the main chain, and thus the fluctuation of the side chain affects, to a varying degree, the state of the conjugated polymers. From this point of view, we should discuss the phase transition of the conjugated polymer with taking into account the complex structure of the conjugated polymer including side chains.

Polydiacetylene (PDA) occupies a position as a prototype in the conjugated polymers, because it is obtained in a single crystal by solid-state polymerization of the monomer crystals [1]. One of the interesting properties of PDA is the phase transition accompanied by beautiful color change [2–4]. The phase transition was discussed in the view of configurational change of the main chain: transformation from acetylene-type $(=CR-C\equiv C-CR=)_n$ to butatriene-type structure $(-CR=C=C=CR-)_n$, where n is the number of monomer units and R denotes the side chain. Resonant

Raman spectroscopy revealed that both frequencies of the $C\equiv C$ and the $C=C$ bonds were shifted to the lower wave-number side than those of the low-molecular-weight compound. Therefore, there is substantial admixture of these configurations at thermal equilibrium [5–7].

The phase transition is related to the change of the conjugation length that is determined by the length π -electron delocalized over. Since the extent of π -electron delocalization along the main chain affects the optical properties of PDA, the dramatic color change is qualitatively explained by this presumption. The change of the conjugation length is accompanied by relaxation of polymer structure including the side-chains, e.g. rotation around the carbon–carbon single bond (C–C). Therefore, the phase transition behavior is presumably affected by the modification of the side-chain structure. However, limited number of experimental effort has been done for making clear the effect of the side chain on the phase transition behavior.

In the present study, we have studied on the visible reflection and mid-infrared (MIR) absorption of PDA with butylene-*N*-difluorophenyl carbamate, $-(CH_2)_4O(CO)(NH)C_6H_4F_2$, as a side chain. In particular, we studied poly-5,7-dodecadiyne-1,12-diol bis[2,4-difluorophenyl carbamate] (PDA-2,4-DFPC) and poly-5,7-dodecadiyne-1,12-diol bis[3,4-difluorophenyl carbamate] (PDA-3,4-DFPC) shown in Fig. 1. These are PDAs obtained by difluorination of phenyl ring at the end of the side chain of poly-5,7-dodecadiyne-1,12-diol

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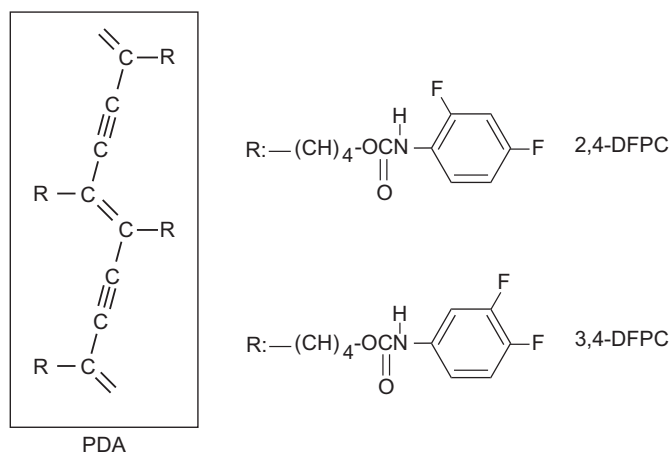


Fig. 1. Structure of a substituted polydiacetylene (PDA), where R denotes the side chain. The side-chain structures for PDA-2,4-DFPC and PDA-3,4-DFPC are schematically illustrated.

bis[phenyl carbamate] (PDA-TCDU). Though PDA-TCDU is polymorphic, the generally obtained form shows no thermochromic phase transition [8]. We found that PDA-3,4-DFPC shows thermochromic phase transition. The results clearly show that the side chain plays a crucial role to establish the structural order in PDA. Moreover, we found that PDA-2,4-DFPC, which is not thermochromic, shows a phase transition exclusively under the photo-excitation. We discussed the correlation between the phase transition and the relaxation of side chain on the bases of the results of the MIR absorption spectroscopy.

2. Experimental methods

The diacetylene monomers were synthesized by the reaction of 5,7-dodecadiyne-1,12-diol with difluorophenyl isocyanates. In the present study, 5,7-dodecadiyne-1,12-diol bis[3,4-difluorophenyl carbamate] (DA-3,4-DFPC) and 5,7-dodecadiyne-1,12-diol bis[2,4-difluorophenyl carbamate] (DA-2,4-DFPC) were synthesized. The crude powder of the monomer was purified by repeated recrystallization from acetone solution. The single crystals of the monomers were obtained from methanol solution by slow evaporation method. The polymerization of the monomer crystals was carried out at room temperature by irradiating X-ray generated from an X-ray source equipped in a conventional X-ray diffractometer (RIGAKU, RINT-2200). After the polymerization, all of the crystals were converted into PDAs without destructing the crystalline shape.

The films peeled off from the PDA single crystals were used as a specimen for the optical spectroscopy. The PDA film was attached on a BaF₂ plate placed on a heating stage in a vacuum vessel. The temperature of the sample was monitored by a thermo-couple clamped at the heat stage. The visible reflection spectra were measured using a coaxial optical fiber bundle comprised from six illumination fibers and a probe fiber. White light from a conventional Xe lamp was guided to the illumination fibers and focused on the sample surface by an achromatic lens. The reflection from the sample was collected by the same lens as the illumination, and guided to a spectrometer comprising a monochromator (Jobin Yvon HR-320) and a CCD (Roper Scientific, NTE/CCD-1340/400-EM) detector. The MIR absorption spectra of the specimens were measured by a system composed from an infrared microscope (JASCO, IRT-5000) and a Fourier transform infrared spectrometer (JASCO FT/IR-6300). The photo-excitation was performed by a green laser (Changchun New Industries

Optoelectronics Tech. Co., Ltd., MLL-III-532). The excitation intensity was adjusted by using neutral density filters. In the visible reflection measurement under the excitation, we inserted a notch filter (Edmund, Rugate Notch Filter 532 nm) into the optical path for avoiding the disturbance by the reflected or scattered laser beam.

3. Experimental results

3.1. Results of visible reflection spectroscopy

In Fig. 2, we show the reflection spectra of PDA-3,4-DFPC and PDA-2,4-DFPC at room temperature, 26 °C, and above 120 °C measured with the polarized light having the *E* vector paralleled to the main chain. At room temperature, both PDA-3,4-DFPC and PDA-2,4-DFPC show the spectra characterized by a sharp peak in the proximity of 1.9 eV. The spectral feature well corresponds to that of the low-temperature phase, which is the so-called blue phase or A phase, of PDA. Hereafter, we denote the low-temperature phase of PDA as A phase. On close inspection, the peak of PDA-3,4-DFPC is at 1.87 eV, while that of PDA-2,4-DFPC is at 1.96 eV. The difference of the peak position is presumably attributed to the difference in the conjugation length. In other word, PDA-3,4-DFPC has longer conjugation length than PDA-2,4-DFPC.

PDA-3,4-DFPC changed its spectrum into that characterized by a peak at around 2.2 eV above 120 °C. The jump of the peak position was nearly 0.3 eV. The spectrum with the 2.2-eV peak is

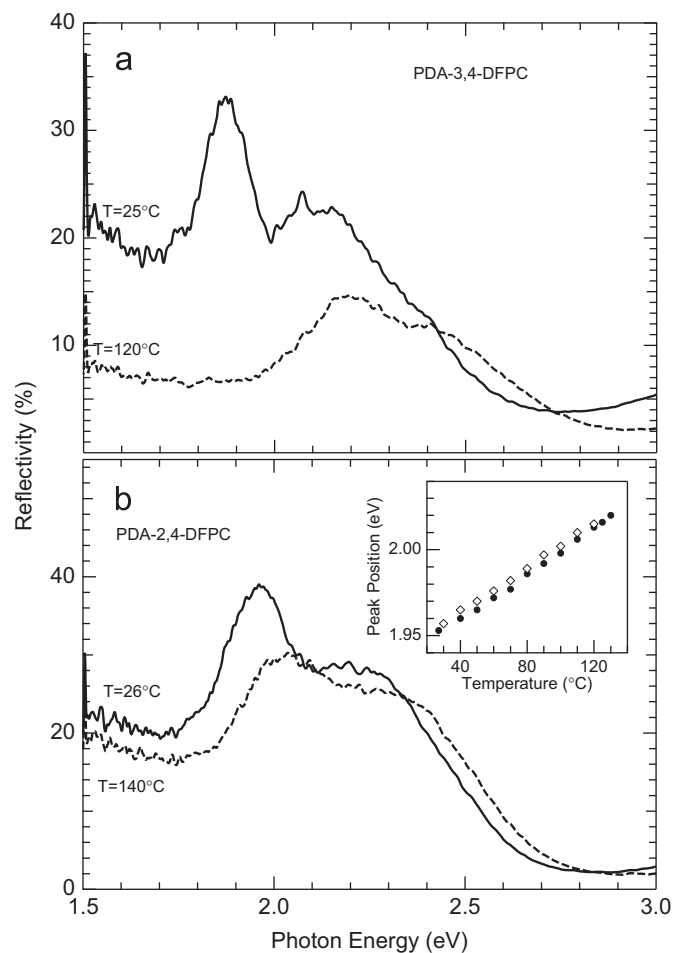


Fig. 2. Visible reflection spectra of PDA-DFPCs: PDA-3,4-DFPC (a) and PDA-2,4-DFPC (b). In the insert figure of the lower panel, the peak position of the reflection spectrum is plotted as a function of temperature.

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