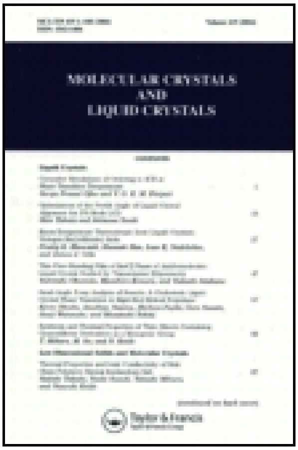

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Electronic Structures of the Polydiacetylene Derivatives Bearing Sulfur Atoms Directly Bound to the Polymer Main Chains

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ELECTRONIC STRUCTURES OF THE POLYDIACETYLENE DERIVATIVES BEARING SULFUR ATOMS DIRECTLY BOUND TO THE POLYMER MAIN CHAINS

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Abstract We synthesized new types of polydiacetylenes (PDAs) bearing alkylthio groups directly bound to the conjugated main chains. Exciton absorption maxima of the obtained PDAs appeared at 750 nm, which was 50 nm longer than those of PDAs substituted with arylthio groups. The stronger electron donating ability of alkylthio substituents led to the smaller energy band gap in those PDAs.

INTRODUCTION

Polydiacetylenes .(PDAs), which are a unique form of conjugated polymers and obtained as large single crystals by solid-state polymerization,[1] have been of interest as 3rd-order nonlinear optical materials. To enhance the nonlinear optical properties of PDAs, we have investigated the possibility of obtaining smaller band gaps in new PDAs by electron donation from the substituents.[2] Recently, we reported a new type of polydiacetylenes bearing arylthio groups directly bound to the polymer main chain.[3-4] The exciton absorption of these polymers appeared at ca. 700 nm, which is longer than those of poly-TCDU (ca. 560 nm) and poly-PTS (ca. 610 nm).

In this paper, to increase the electron donating effect from the substituents, we designed new PDAs having alkythio groups directly bound to the π-conjugated main chain because alkylthio groups are thought to have stronger electron donating ability than that of arylthio groups. The syntheses, the electronic states, and the third harmonic generation of the new polydiacetylenes are reported.

EXPERIMENTAL

Monomers (**1a-d**) were synthesized according to the same manner described in our previous paper.[3] All of monomers (**1a-d**) shown in Fig. 1 were obtained as white color crystals (m.p. ; **1a**=66.2℃, **1b**=49.9℃, **1c**=50.4℃, **1d**= 66.3℃).

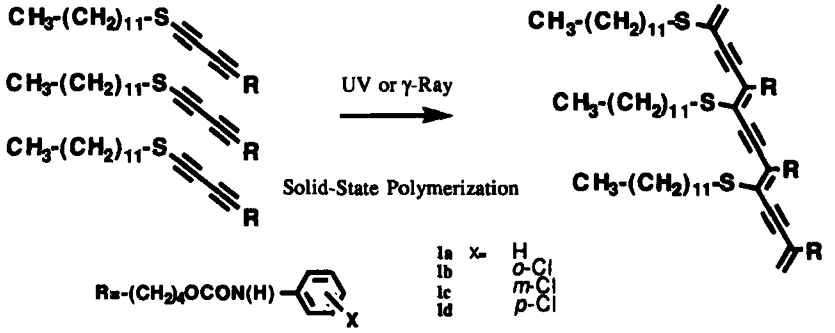

FIGURE 1 Chemical structures of the synthesized polydiacetylenes and the schematic representation of the solid-state polymerization.

The solid-state polymerization of the diacetylenes was performed with the exposure to UV light (254 nm) or γ-rays (^{60}Co, 0.15 MR/h), and the polymer yields were evaluated by the change of carbon-carbon triple bonds stretching band in the IR spectra (KBr) or by weighing residue after rinsing powder samples with benzene.

The X-ray diffraction (XRD) spectra were recorded to check the crystallinity after polymerization. The absorption spectra and the third-harmonic generation were measured. The thin films of monomer were prepared by spin coating from chloroform solution and polymerized by UV irradiation. The $\chi^{(3)}$ values of the **poly-1d** (film thickness = 0.015 μm) were determined by the THG Maker fringe technique using fused silica ($\chi^{(3)} = 1 \times 10^{-14}$ esu) as a reference.[5]

RESULTS AND DISCUSSION

The white crystals of synthesized diacetylenes (**1a-d**) became deep blue by UV exposure. According to the previous papers,[1-4] this phenomenum suggests that solid-state polymerization occurred in the diacetylenes. Furthermore, in the IR spectrum, absorption at 2120 cm^{-1} decreased while that at 2061 cm^{-1} increased. The former and the latter are identified to be the carbon-carbon triple bonds stretching of the monomer and the polymer, respectively. As shown in Fig. 2, the yields of insoluble polymers reached almost 100% by γ-ray irradiation to the monomer (**1a-d**). From these results we concluded that the synthesized diacetylenes (**1a-d**) could be

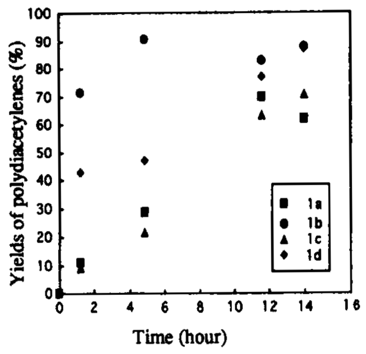

FIGURE 2 Time conversion curves of the solid-state polymerization by γ-ray.

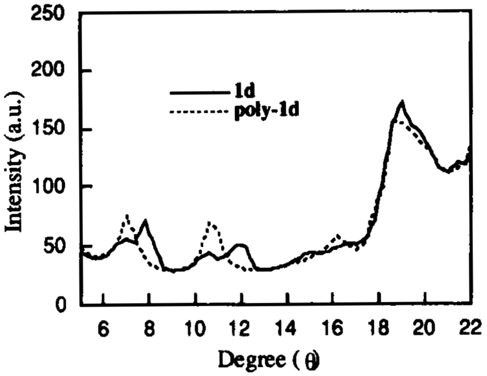

FIGURE 3 XRD spectra of **1d**.

topochemically polymerized in the manner of 1,4-addition as shown in Fig. 1.

In Fig. 3, the change in the XRD spectra was observed in the course of X-ray irradiation and also the color of monomer turned to deep-blue. This means that solid-state polymerization occurred by X-ray irradiation. The diffraction peaks were very broad and the shift of the peaks at ca. 8 and 12 degree were very large after polymerization. From this result, we could estimate that the solid-state polymerization did not proceed in an ideal topochemical and topotactic manner. On the other hand, previously reported analogous PDA having *p*-bromophenylthio groups (**poly-2d**)[3] could be obtained as perfect crystals whose structure could be solved by X-ray analysis.[6] Compared with **poly-2d**, the long alkyl chain may introduce the loose crystal packing and cause the large movement of molecules during solid-state polymerization.

In Fig. 4, the exciton absorption maximum of **poly-1d** appeared at ca. 750 nm, which was about 50 nm red shifted from that of **poly-2d** having *p*-bromophenylthio groups. This red shift of the exciton absorption maximum might be due to the stronger electron donation of alkylthio groups to the polymer main chain than *p*-bromophenylthio groups. These results suggest that the electron donation of sulfur atoms was effective in altering the electronic structures of the PDAs. Thus **poly-1d** has a different electronic structure from conventional PDAs, such as poly-TCDU (ca. 560 nm) and poly-PTS (ca. 610 nm).

compared to the values of conventional PDAs, demonstrating that the third-order nonlinear optical properties can be enlarged through an increase of the electron densities in the π-conjugated main chains.

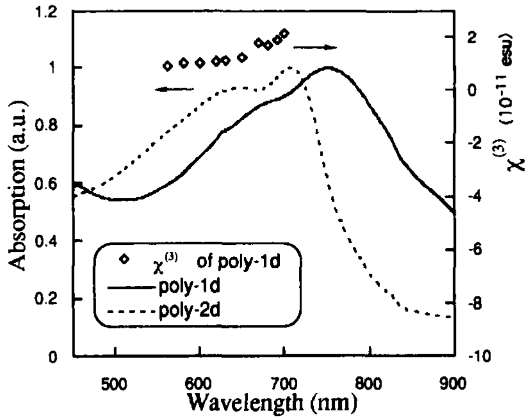

FIGURE 4 Absorption spectra of **poly-1d** and **poly-2d** and $\chi^{(3)}$ values of **poly-1d**.

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