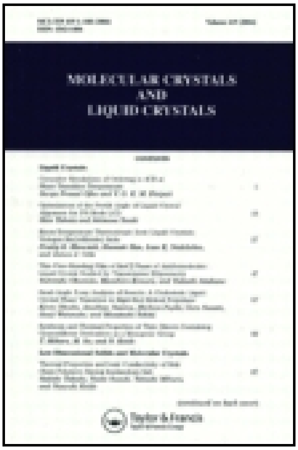

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Two different sorts of π-conjugated systems, polydiacetylene and tetrathiafulvalene, were regularly assembled in a "hybrid" organic crystal using the solid-state polymerization of the corresponding diacetylene monomers. The absorption spectra and the electro-conducting properties of the polydiacetylene obtained as a "hybrid" crystal were reported.

Keywords: Polydiacetylene, Solid-state polymerization, Tetrathiafulvalene, Electro-conductivity, Charge transfer complex,

INTRODUCTION

Polydiacetylenes (PDAs) are a unique form of π-conjugated polymers which can be obtained as large single crystals by topochemical solid-state polymerization.[1] The topochemical reaction can be described as a diffusionless transformation of the parent crystal into the daughter crystal. The unique feature of the reaction is that it proceeds within the monomer lattice and, being completely controlled by the packing of the monomer, affords to the π-conjugation crystals. Therefore, PDAs have almost the largest thirdorder nonlinear optical properties ($\chi^{(3)}$) among many organic compounds, which due to the perfectly aligned π-conjugated polymer main chain.[2] The $\chi^{(3)}$ values along the polymer main chain were evaluated using the thin single crystals obtained by share growing or cutting techniques.[3,4] It reaches to be 10^{-6} esu order in one-photon resonance.[5] Such thin single crystal formation is often difficult to make a material with good optical quality. Accordingly, nano-meter size microcrystals of PDAs are also prepared to obtain a uniform composite material, whose nonlinear optical properties were confirmed by z-scan measurement to be as large as those of PDA single crystals.[6,7]

In addition, the modified π-electron systems can be designed by using the diacetylene solid-state polymerization because of the stereo-regularly reaction mentioned above. For example, to obtain the longer absorption maxmum of PDA exciton, we have synthesized several types of new PDAs with increased number of π-electrons per repeating unit.[8] As the planer π-conjugation of the main chain are regularly maintained in the crystal, the perturbation of carbon conjugated chain affected by the electron donating or withdrawing effect of substituents, e.g. phenyl groups, acetylenic groups, or hetero atoms as shown in Figure 1, can be observed as absorption spectral shifts. In the case of PDA substituted with phenyl groups, it is clearly demonstrated that the excitonic absorption maxima increase with decreasing the dihedral angles between the main chain and phenyl rings.[9] In the most recent study, PDA having alkythio groups directly bound to the polymer main chain showed the longest red-shift of the excitonic absorption peak, which was at ca. 750nm.[10]

Although the large electron mobility of PDA in the chain direction has been reported,[11] the electric conductivity is fairly low because of the small number of charge carriers. Meanwhile, tetrathiafulvalene(TTF) derivatives and

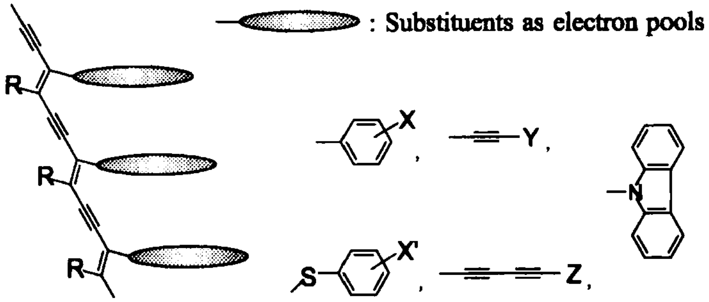


FIGURE 1 Polydiacetylenes with π-conjugation between the main chain and the substituents.

their highly conductive charge-transfer complexes have attracted much attention. Therefore, we have been interested in the incorporation of TTF moieties into the PDA crystals. Such a molecular design would have regularly mixed π-systems of PDA main chain and TTF column. It could be so-called a "hybrid" organic crystal or π-system super-lattice as shown schematically in Figure 2. In this paper, as the first trial of such molecular architecture, we report the synthesis of PDA containing TTF moieties and their electrical properties.

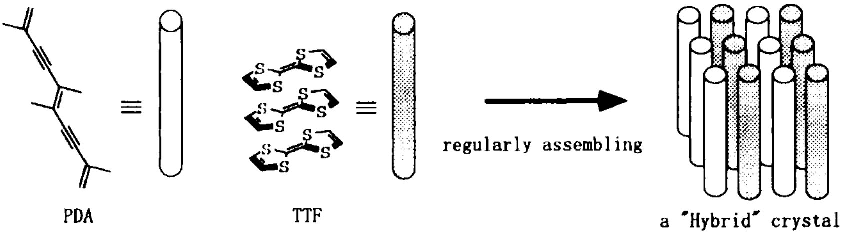
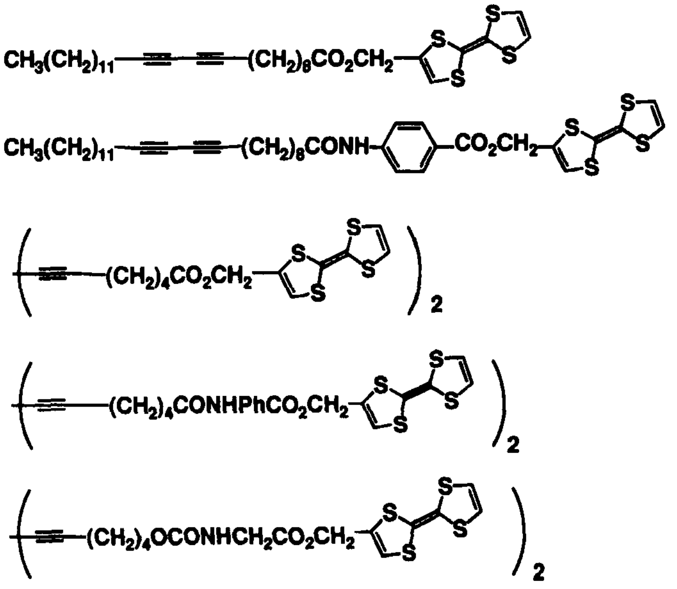


FIGURE 2 Schematic representation of molecular architecture for a regularly mixed π-systems in a "hybrid" crystal.

DESIGN OF SOLID-STATE POLYMERIZATION

TTF moieties were introduced to diacetylene monomers by esterification reaction of 4-(hydroxymethyl)tetrathiafuluvalene.[12] According to the crystal engineering of molecular packing for solid-state polymerization, several diacetylene monomers as shown in Figure 3 were synthesized, which had amide, urethane, ester group and/or long alkyl chain. Among these derivatives, only compound 1 and 2 could be polymerized by UV-irradiation in the solid-state. From this result, it is concluded that the long alkyl chain in the unsymmetrical diacetylenes plays an important role to crystallize in a polymerizable stack. The details of the synthesis will be published elsewhere.[13] The polymerization behavior and properties only for compound 1 was hereafter described and for compound 2 also in a similar manner as compound 1.



1

2

3

4

5

FIGURE 3 Chemical structures of diacetylenes having TTF moieties.

The color of the crystals of compound 1 changed to dark blue from yellow after exposure to UV with a low-pressure mercury lamp or ^{60}Co γ-ray irradiation as shown in Figure 4. The spectrum was measured using a KBr pellet dispersed with crystallite of compound 1. The absorption maximum at 630nm is the same as that of the typical PDAs. After the crystal is thus colored, X-ray diffraction pattern still show almost the same as that of the monomer. Furthermore, the spectrum of solid-state ^{13}C-NMR is consistent with the PDA main chain structure.[14] The polymer conversion is saturated at about 70% after γ-ray dose of 300KGy. The obtained bluish polymer 1 can not be dissolved in common solvent, but using polar solvents, e.g. dimethyl formamide or dimethyl sulfoxide, at the boiling point the polymer became soluble. After the polymer 1 was once dissolved at such high temperature, even at ambient temperature the reddish color solution was stable.

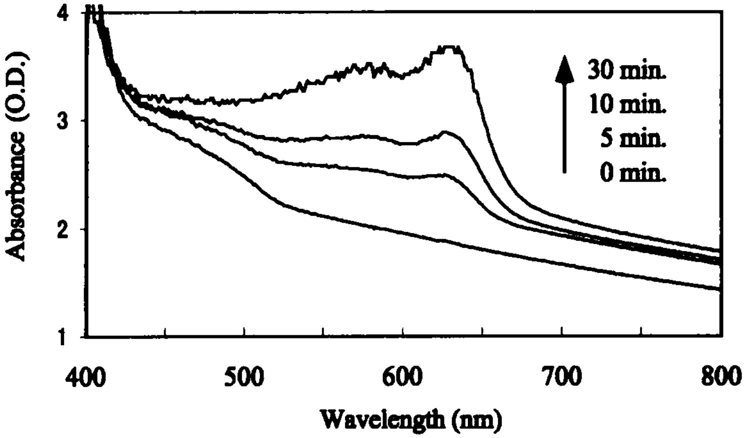


FIGURE 4. Absorption spectral change of compound 1 in the course of UV-irradiation.

As the absorption maximum of the solution is at 540nm, which is ca. 90nm blue shift from that of the crystal, the conformation of polymer main chain are disturbed by dissolving. The reddish color reversibly turned to yellow when the temperature rose. This thermochromism is due to the typically reversible helix-coil transition of PDA main chain.[15]

REDOX AND ELECTRICAL PROPERTIES

The cyclic voltammetry of compound 1 and TTF was shown in Figure 5. The redox behavior of compound 1 is completely the same as that of TTF,[16] which exhibits two reversible redox couples at $E^{1/2}_1$ +0.3 and $E^{1/2}_2$ +0.67 V vs. SCE in acetonitrile. Unfortunately, the cyclic voltammetry of polymer 1 gave no peak because of too small concentration of the solution. However, polymer 1 formed the charge-transfer (CT) complex with TCNQ in the solution and the CT band strongly appeared at 750 and 850nm. Furthermore, TTF skeletons were confirmed by IR and NMR spectral measurements after UV or γ-ray irradiation. From these results, it proved that TTF moiety was incorporated in the structure of polymer 1.

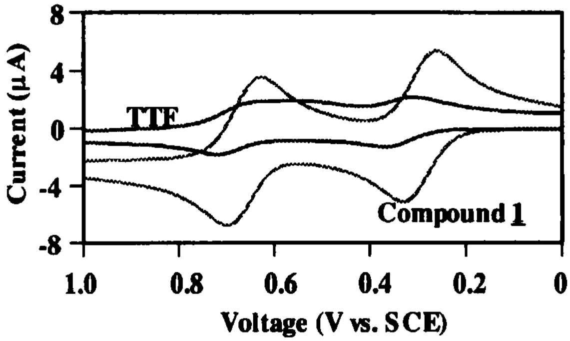


FIGURE 5 Cyclic voltammetry of compound 1 and TTF in acetonitrile with Bu_4NPF_6 electrolyte.

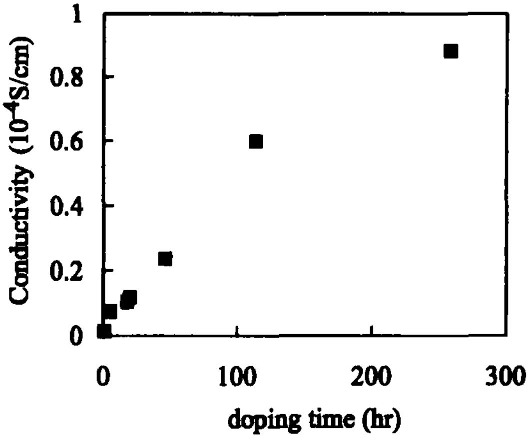


FIGURE 6 Conductivity change of polymer 1 in the course of I_2 doping.

The electro-conductivity was measured by a four-point electrode method *in vacuo* using a powder crystalline sample pelletized into a disk. The polymer 1 is insulator with the conductivity less than 10^{-10}S/cm. Exposing the disk sample upon iodine vapor, the conductivity rapidly increased to be 10^{-5} S/cm, and then, gradually attained to 10^{-4}S/cm order as shown in Figure 6. It has been already reported that PDAs, which have the nearly perfect crystal lattice, can not be doped with any chemicals,[17] and even PDAs with a less perfect lattice, e.g. an amphiphilic PDA in multilayer and so on, are doped with iodine up to a conductivity of 10^{-6}S/cm.[18] Therefore, the electro-conductivity of polymer 1 doped with iodine is owing to the CT complexes of TTF and iodine. In the solution mixture of polymer 1 and iodine, the CT band was observed at 600nm. Namely TTF moieties incorporated in PDA crystals can form a electro-conducting pass upon chemically doping.

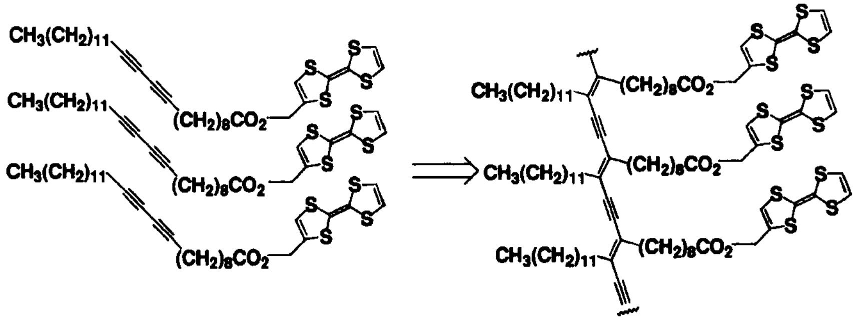


FIGURE 7 Solid-state polymerization scheme of diacetylene having TTF moiety via 1,4-addition.

CONCLUSION

Several new diacetylene monomers having TTF moieties were synthesized and among them only compound 1 and 2 could be polymerized in the solid-state, proceeding via 1,4-addition. As a result of this solid-state polymerization, we preliminary succeeded in the first trial of molecular architecture to obtain a "hybrid" crystal, where two different π-systems were regularly assembled as shown in Figure 7. Desired more interesting molecular architecture, the solid-state polymerization of diacetylene should be proceeded after the forming a regular CT column of TTF and acceptor, e.g. TCNQ. In such a molecular super-lattice combined with metallic and excitonic wires a quantum effect between such two different sort of quasi one-dimensional π-electron systems should be expected, however, it has not yet succeeded that the CT diacetylenes stack into a solid-state polymerizable crystal. We consider that an electrochemical oxidation, which is the same old trick of the preparing CT crystals, should be promised to realize such molecular architecture for PDA combined with CT of TTF. Such the second trials will be in progress using all new diacetylene-TTF compounds because there is a possibility to stack in solid-state polymerizable crystals after the formation of CT complex.

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