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A New Fused-Ring Conjugated Polymer. Di(polydiacetylene)

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A new conjugated polymer which has π-conjugation between two polydiacetylene backbones was synthesized by two-step solid-state polymerization of a dialkyltetraacetylene compound. This polymer is considered to be a fused-ring polymer of conjugated 10π-electron system.

Conjugated polymers like polydiacetylenes,[1] polyacetylenes,[2] and polythienylenes[3] have attracted much attention for their superior third-order nonlinear optical properties. To achieve enlarged third-order susceptibilities by increasing the π-electron numbers per repeating unit, we have synthesized polydiacetylenes having π-conjugation between polymer backbone and side chains.[4] In our recent studies, we have reported that dialkyltetraacetylene compounds can be polymerized in the solid-state via unsymmetrical 1,4-addition to give diacetylene-substituted polydiacetylenes in quantitative yield, and the resultant polymer surely has π-conjugation between the backbone and the side chains.[5,6] Since the polymer has diacetylene moieties in the side chains, their solid-state polymerizability and resulting polymer structure have been investigated in the present study.

The monomer used was hexatriaconta-15,17,19,21-tetrayne. In the first step of solid-state polymerization, the monomer crystals were irradiated by γ-ray of *ca.* 30 Mrad at room temperature to give a polydiacetylene having a tetradecyl group as a substituent and an octadeca-1,3-diynyl group as the other substituent in a repeating unit (polymer 1).[6] The second step of solid-state polymerization was stimulated by thermal treatment at 100 °C for one day under a nitrogen atmosphere to give polymer 2.

Figure 1 shows the IR spectrum of polymer 2. Closer examination in

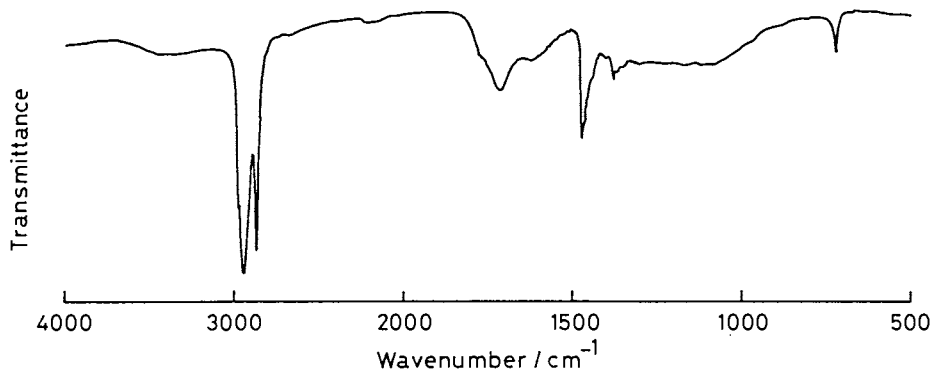

Fig. 1. IR spectrum of polymer 2 (KBr).

comparison with that of polymer 1 reveals that $\nu_{C\equiv C}$ of polymer 1 at 2114 and 2237 cm^{-1} disappeared and new broad bands in the region of 1500-1800 cm^{-1} appeared in the course of the second step of polymerization. These broad bands must correspond to the stretching vibrations of newly-formed carbon-carbon multiple bonds. No changes in the absorption bands corresponding to long-alkyl groups were observed between polymers 1 and 2.

Figure 2 shows the solid-state ^{13}C-NMR spectrum of polymer 2, together with that of polymer 1. According to the detailed characterization,[6] the peaks of polymer 1 at 147.3 and 110.5 ppm correspond to two olefinic carbons of the polymer backbone, those at 105.0 ppm to overlapped two acetylenic carbons of the polymer backbone and those at 89.5, 80.6, 72.7, and 65.2 ppm to four acetylenic carbons of the side chains. In the spectrum of polymer 2, all these peaks disappeared and two very broad peaks around 145 and 80 ppm are observed. The two broad peaks can be regarded as

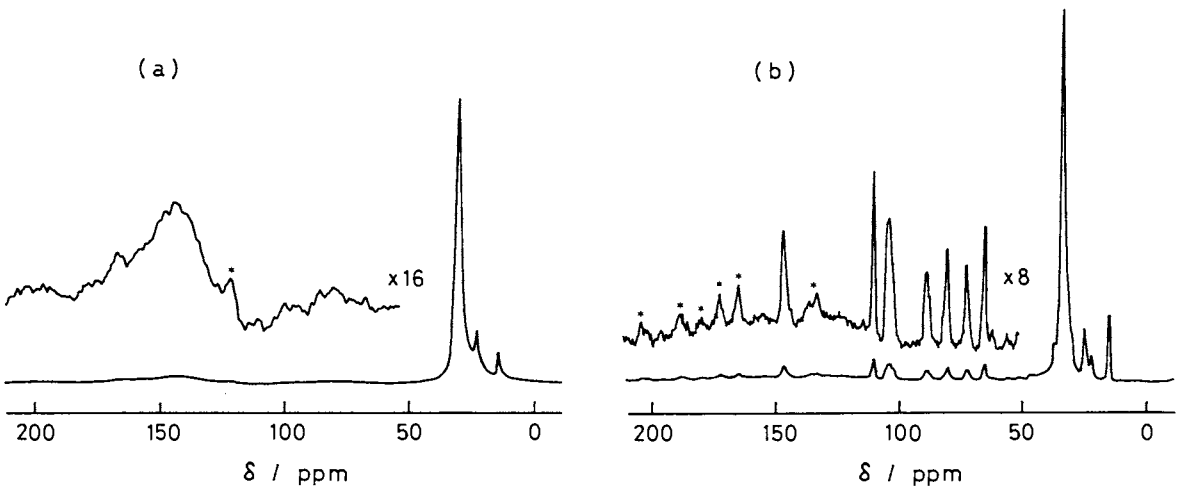

Fig. 2. Solid-state ^{13}C CP/MAS spectra of polymers 2 (a) and 1 (b). Asterisks indicate spinning side bands.

olefinic and acetylenic carbons, respectively. Peak broadening may be due to thermal disordering of polymer crystals in the second step of polymerization. It should be noted that the peak of polymer 1 at 22.2 ppm which corresponds to the methylene attached to the diacetylene moiety of the side chain also disappeared in polymer 2. This suggests that different circumstances of the two alkyl groups in polymer 1 become equivalent in polymer 2.

From all these results, it is estimated that the solid-state polymerization of polymer 1 proceeds also via 1,4-addition to give another polydiacetylene backbone directly bound to the former one, as shown in Fig. 3. The resultant di(polydiacetylene) can be considered as a fused-ring polymer of conjugated 10π-electron system.

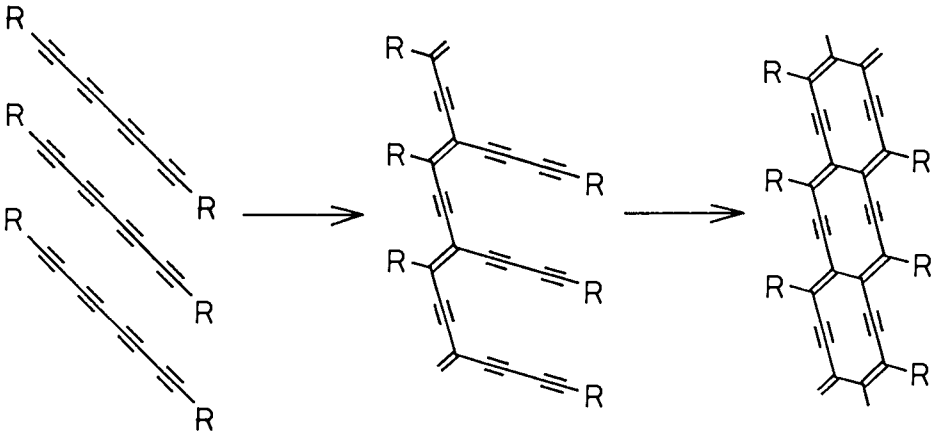

Fig. 3. Two-step solid-state polymerization scheme from tetraacetylene monomer to di(polydiacetylene) (polymer 2) via diacetylene-substituted polydiacetylene (polymer 1).

Actually this structure was also supported by the peculiar dichromism under a polarizing microscope. In the case of polymer 1, the colors of the polymer crystallite under the polarization along and across the polymer backbone were deep blue and almost colorless, respectively, as were the cases of other conventional polydiacetylene crystals. However, in the case of polymer 2, the colors were dark reddish orange and thin orange. This thin orange color clearly indicates the existence of any longer π-conjugation, even perpendicular to the polymer backbones, just like the structure of polymer 2 in Fig. 3. The dark reddish orange color along the polymer backbone is understandable in analogy to the well-known polyacene.[7)]

In conclusion, we have succeeded in the first synthesis of a fused-ring polymer of conjugated 10π-electron system from a tetraacetylene compound. The measurements of optical and electronic properties and synthetic expansion are currently in progress.

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