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A New Conjugated Ladder Polymer Synthesized by Solid-State Polymerization of a Hexayne Compound

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A new conjugated ladder polymer, in which two polydiacetylene backbones are connected by a butadiynylene group at every repeating unit, was synthesized by spontaneous solid-state polymerization of a dialkylhexayne compound at room temperature.

Polydiacetylenes are known as a unique class of conjugated polymers obtained by topochemical solid-state polymerization,[1] and are considered to be one of good candidates for the third-order nonlinear optical materials.[2] In the series of our studies to enlarge the third-order nonlinear optical susceptibilities of polydiacetylenes by increasing π-electron numbers per repeating unit, we have investigated polydiacetylenes having π-conjugation between a polymer backbone and side chains.[3,4] Among them, especially interesting are the polymers from conjugated tetrayne compounds, i.e. the polydiacetylenes with diacetylenic groups directly bound to the main chain.[4] Further polymerization of the diacetylenic group in the side chains is estimated to give the di(polydiacetylene)s, which are conjugated ladder polymers composed of two polydiacetylene backbones and are also said to be a fused-ring polymer of 10π-electron system.[5] In the present study, we extended the conjugated monomer system to a hexayne compound, and investigated its solid-state polymerization behavior.

In order to simplify the structure analysis, an alkyl-substituted hexayne monomer of 15,17,19,21,23,25-tetracontahexayne[6] was synthesized in our laboratory. Polymerization of this hexayne compound started

spontaneously at ambient temperature even without light or γ-ray irradiation. Color of the polymer in the initial stage of polymerization was green, i.e. the largest absorption maximum was observed around 770nm. Then, crystals gradually became black. Since the high-resolution solid-state ^{13}C-NMR spectroscopy is a powerful tool for the structure analysis of this kind of compounds,[4] polymer structures during polymerization were continuously monitored by ^{13}C-NMR spectra under cross-polarization and magic angle spinning conditions. After recrystallization of the monomer,

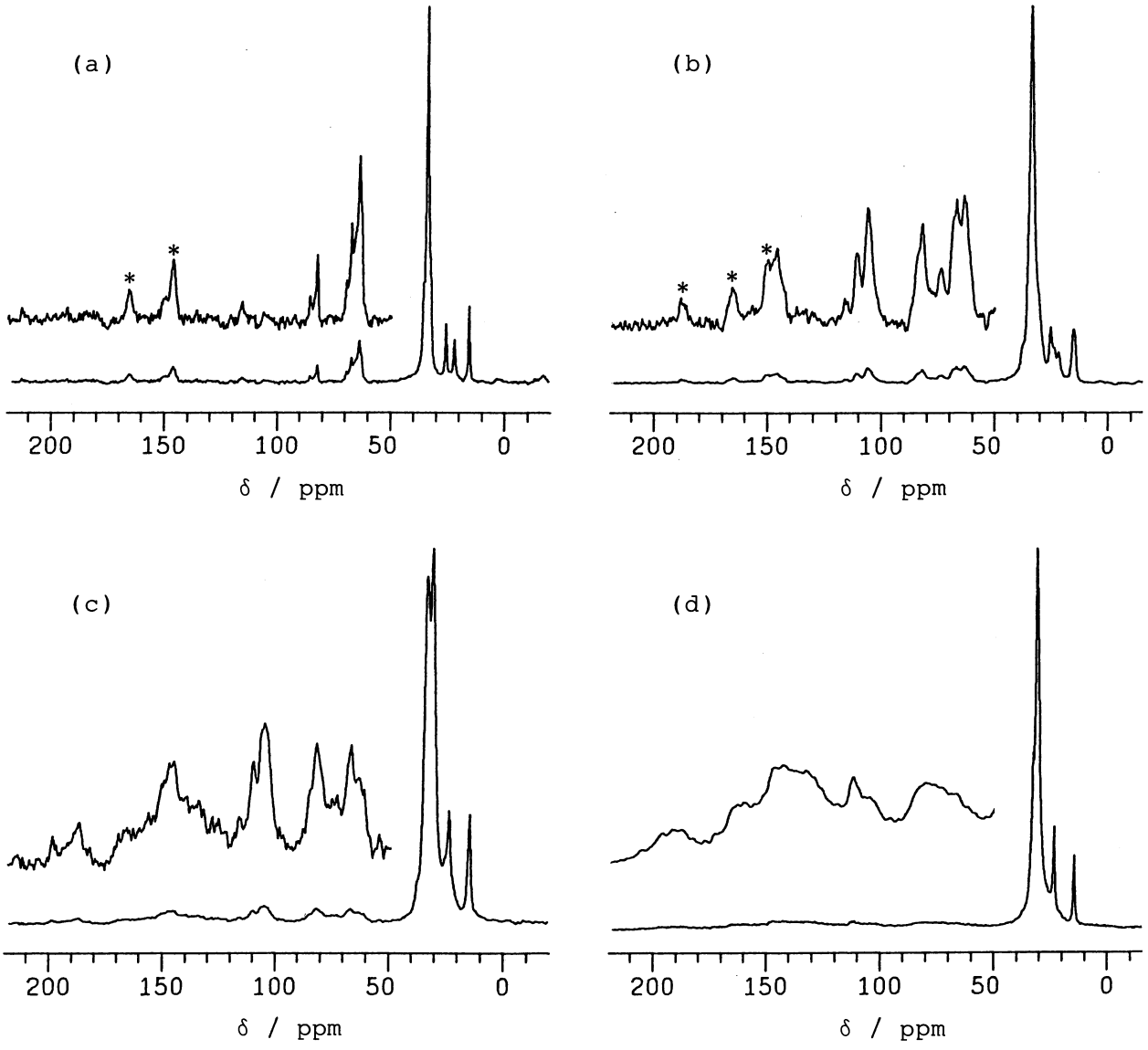

Fig. 1. Spectral changes in solid-state ^{13}C-NMR spectra of a hexayne. The figures (a), (b), (c), and (d) are the spectra recorded after 0.5 h, 22 h, 56 h, and 11 days, respectively. Asterisks indicate spinning side bands.

crystals were immediately packed in a rotor for the NMR measurement. The starting point of the reaction time was set to the beginning of the recrystallization of the monomer. Experimental detail will be reported elsewhere soon.[7)]

Figure 1 shows the ^{13}C-NMR spectral change of the hexayne compound during polymerization. The spectrum (a) is for the monomer. Smaller peaks around 82 ppm are for acetylenic carbons bonded to an alkyl chain and larger peaks around 62-69 ppm are for other ten acetylenic carbons. Fine splitting of these peaks may be due to the polymorphism of the monomer.

The spectrum (b) was recorded after 22 h. Characteristic peak patterns for carbons of an unsymmetrically-substituted polydiacetylene backbone[4)] were recognized in the region from 110 to 150 ppm, i.e. the peaks at 146 and 111 ppm correspond to the olefinic carbons attached to the alkyl and the acetylenic side chains, respectively, and the peak at 106 ppm to overlapped two acetylenic carbons. Peaks from 55 to 85 ppm correspond to the acetylenic carbons in the side chain.

After 56 h, peak area of backbone carbons increased, though that of acetylenic carbons in side chains decreased as shown in the spectrum (c). This indicates that acetylenic groups in side chains were polymerized to give another polydiacetylene backbone. In the side chain region, split peaks of the spectrum (b) seem to be combined with two broad peaks at 67 and 82 ppm. From the higher symmetry of the spectrum (c), the polymer is considered to have the structure where two polydiacetylene backbones are connected by a butadiynylene group at every repeating unit.

The spectrum (d) was recorded after 11 days. All the peaks corresponding to quaternary carbons were broadened, and new broad peaks around 125-140, 160 and 190 ppm appeared. There are no suitable peaks assigned to hydrocarbons for the latter two peaks except allenic carbons. Thus, the polydiacetylene backbone structure seems to be gradually changed from ene-yne to triene structures.

The polymerization scheme of a hexayne with alkyl substituents is summarized in Fig. 2. In the first step of solid-state polymerization, a hexayne monomer is polymerized at the 1,4-position of hexayne to give a polydiacetylene substituted by alkyl and octatetraynyl groups (polymer 1). In the second step, the polymerization occurs at the 9,12-position of the original hexayne moiety to give a ladder polymer of two polydiacetylenes bonded by butadiynylene groups (polymer 2). In the last step, allene structures are produced in the ladder polymer, and plausible structures are estimated to be the trienes in polydiacetylene backbones (polymer 3). Synthesis of the related compounds and the measurement of the physical properties are currently in progress.

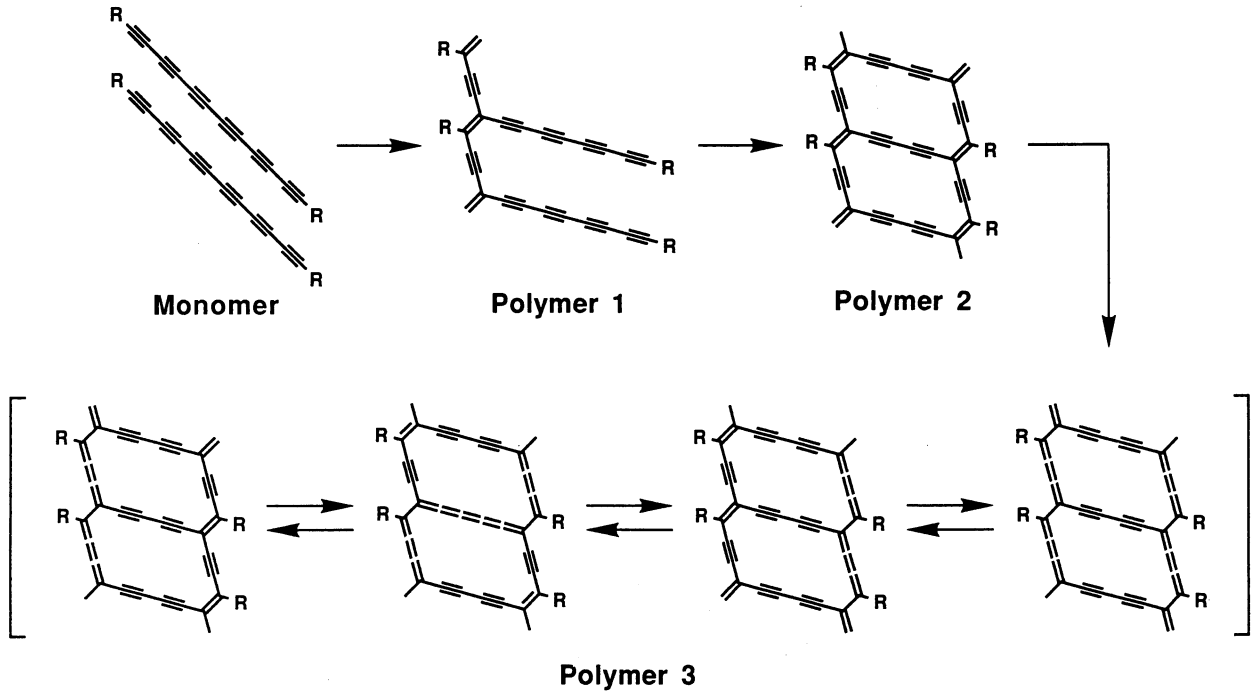

Fig. 2. Polymerization scheme of a dialkylhexayne compound.

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6) 15,17,19,21,23,25-Tetracontahexayne: Mp 78-79 ^{o}C; IR (KBr), 2959, 2924, 2849, 2203, 2169, 1462, 725 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$), δ = 0.88 (6H, t, J = 6.8 Hz), 1.10-1.45 (44H, m), 1.55 (4H, tt, J = 7.1, 7.1 Hz), 2.32 (4H, t, J = 7.1 Hz); ^{13}C-NMR ($CDCl_3$), δ = 14.14, 19.52, 22.69, 27.83, 28.82, 28.98, 29.36, 29.40, 29.54, 29.62, 29.64, 31.92, 60.34, 61.46, 62.36, 62.70, 65.61, 81.91. Found: C, 88.89; H, 11.05%. Calcd for $C_{40}H_{58}$: C, 89.15; H, 10.85%.

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