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Solid-State Polymerization of 15,17,19,21,23,25-Tetracontahexayne

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ABSTRACT: A dialkyl-substituted dodecahexayne derivative of 15,17,19,21,23,25-tetracontahexayne (THY) was found to polymerize spontaneously in the solid state at ambient temperature without irradiation. The polymerization of the THY crystals was monitored by IR and visible–near IR absorption, ^{13}C NMR and ESR spectra, and X-ray diffraction. The following polymerization scheme is proposed. First, a polydiacetylene substituted by alkyl and 1,3,5,7-alkatetraynyl groups is formed by 1,4-addition polymerization of the dodecahexayne moiety. Next, polymerization occurs at the 9,12-positions (on the opposite side) of the original dodecahexayne moiety to give a ladder polymer of two polydiacetylenes bonded by butadiynylene groups. Finally, allene and open shell structures are produced in the ladder polymer.

Introduction

Polydiacetylenes are obtained as single crystals by topochemical solid-state polymerization of the monomer single crystals.[1] They have received considerable attention because of their one-dimensionally π-conjugated structure.[2,3] Their unique π-electron structures and therefore superior third-order nonlinear optical properties have been extensively investigated.[4–7] In our previous studies, we have synthesized various polydiacetylenes with π-conjugation between the polymer backbone and side chains,[8–14] since narrower band gaps and resulting enhanced optical nonlinearities were expected.[15,16] Among them, polydiacetylenes having acetylene substituents directly bound to the main chain[11–14] are interesting, as it is anticipated that complete π-orbital overlap between the main chain and substituents may occur. The monomers for such polydiacetylenes, hexatriyne and octatetrayne derivatives with long alkyl substituents, were synthesized, and their polymerized structures were determined to be polydiacetylenes with 1-alkynyl and alkyl groups and those with 1,3-alkadiynyl and alkyl groups, respectively.[17] For example, the polymerization scheme of 15,17,19,21-hexatriacontatetrayne (HTY) (**1**), an octatetrayne monomer, to the polydiacetylene with butadiynyl substituents **2** is presented in Figure 1. It was found that solid-state polymerization for these monomers always proceeds by 1,4-addition. Further, polydiacetylene **2** could be thermally reacted.[18,19] For the structure of the final polymer, we proposed the ladder polymer **3** where the repeating unit is 1,6-didehydro[10]annulene (**4**), i.e. two conjugated polydiacetylenes. However, the annulene **4** is expected to be unstable.[20] In fact, its cycloaromatization reaction to the 1,5-dehydronaphthalene diradical **5** was recently reported.[21] The instability is considered to be due to in-plane repulsion of the faced π-orbitals at sp-carbons in the annulene ring. Thus, the final structure of the polymers from octatetrayne derivatives after the thermal reaction may be either a planar cycloaromatized polymer and/or a three-dimensional polymer, which would be obtained if the polymerization proceeded in a direction different from that of the same column of the polymer side chain. To obtain the ladder polymer where two polydiacetylenes are conjugated in each repeating unit. It is necessary to keep the polydiacetylene backbones separated by conjugated divalent groups. Similar polydiacetylene ladder polymers without π-conjugation between two polymer backbones, e.g. connected by methylene-type chains[22–25] or a metal,[26] have already been reported to be stable.

In the present study, a dodecahexayne derivative with long alkyl substituents, i.e. 15,17,19,21,23,25-tetracontahexayne (THY), was synthesized as an extended system of octatetrayne derivatives.[27] Its solid-state polymerization behavior was investigated using IR and visible–near IR absorption, NMR, ESR, and X-ray diffraction. We emphasize that solid-state high-resolution ^{13}C NMR spectroscopy is a powerful tool for the structure analysis of polydiacetylenes.[17,23,28–30] THY is particularly attractive because of its potential for forming the polydiacetylene ladder polymer.

Experimental Section

Synthesis of the Monomer. THY (**6**) was synthesized according to Figure 2. Synthesis of 1,3-octadiyne (**10**) from 1-hexadecyne (**7**) was reported previously.[12] Details of the synthesis of **6** from **10** were as follows.

Preparation of 2-Methyl-3,5,7-docosatriyn-2-ol (11). To a solution of **10** (3.69 g, 15 mmol) in a mixture of ethanol (10 cm^{3}) and 2-aminopropane (10 cm^{3}) with 100 mg of copper(I) chloride was added 4-bromo-2-methyl-3-butyn-2-ol (**8**) (3.67 g, 22.5 mmol) in ethanol (10 cm^{3}) dropwise for 1 h at ambient temperature under a nitrogen atmosphere. When the solution became blue by the addition of **8**, hydroxylamine hydrochloride was added until the solution became yellow. After addition of **8** was complete, the solution was stirred for 2 h and the solvent removed under reduced pressure. Diluted hydrochloric acid was added to the residue, and it was extracted with chloroform. The extract was dried with anhydrous sodium sulfate, and the chloroform was removed by vacuum evaporation. The residue was purified using column chromatography (silica gel, benzene) to give 1.57 g (32%) of **11** as crystals: mp 40–42 °C; IR (KBr) 3322, 2994, 2923, 2857, 2217, 2118, 1473, 1344, 1206, 1167, 961, 724 cm^{-1}; ^{1}H NMR (360 MHz, CDCl$_3$) δ 0.88 (3H, t, J = 6.5 Hz), 1.15–1.43 (22H, m), 1.48–1.63 (2H, tt, overlapped with methyl groups), 1.53 (6H, s), 1.97 (1H, broad), 2.29 (2H, t, J = 7.0 Hz); ^{13}C NMR (CDCl$_3$) δ 14.09, 19.38, 22.66, 27.96, 28.79, 29.00, 29.33, 29.41, 29.54, 29.63, 29.66, 30.97, 31.89, 58.84, 64.46, 65.34, 65.57, 67.61, 80.74, 81.28.

Preparation of THY (6). To a solution of **11** (1.312 g, 4 mmol) in benzene (50 cm^{3}) was added powdered potassium hydroxide (224 mg), and the mixture was refluxed for 1 h. After filtration, solvent evaporation and addition of hexane were

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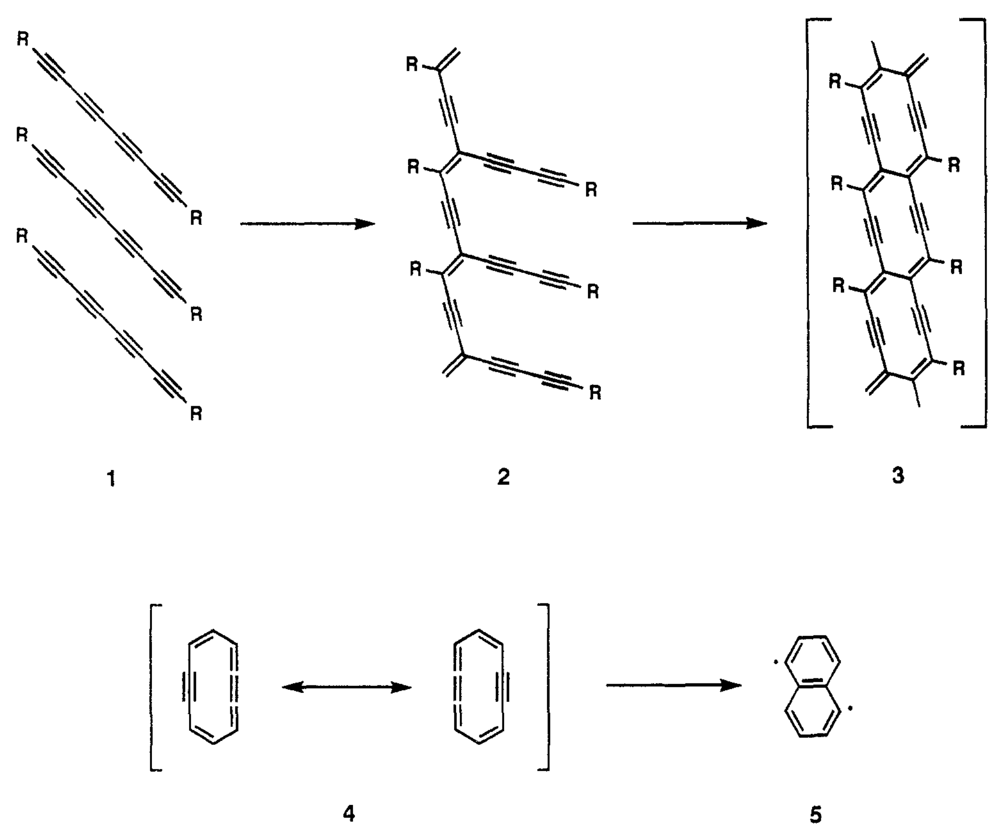

Figure 1. Polymerization scheme of octatetrayne derivatives, where the substituent R is a tetradecyl group for HTY, and cycloaromatization of 1,6-didehydro[10]annulene.

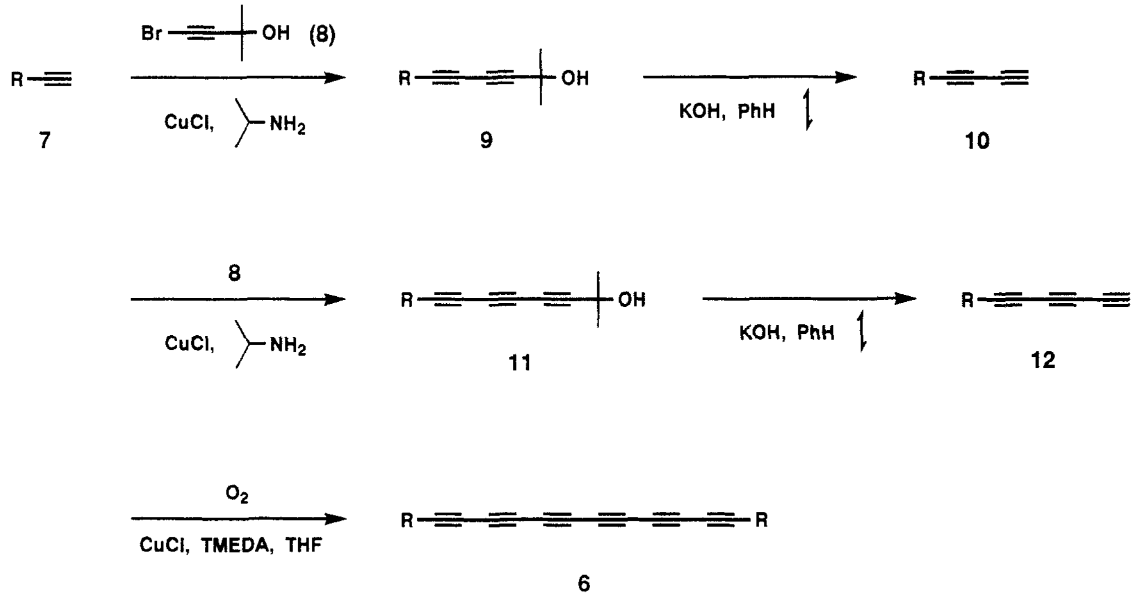

Figure 2. Synthetic procedure of THY, where the substituent R is a tetradecyl group.

alternately repeated to change the solvent from benzene to hexane. Throughout this operation, complete evaporation of the solvent was avoided. Then the concentrated hexane solution was purified by column chromatography (silica gel, hexane) to give 1,3,5-eicosatriyne (12) in hexane. Since 12 can be easily polymerized in its pure oily state, 12 was stored in solution and used as soon as possible. Spectroscopic data for 12 were as follows: IR (film) 3322, 2933, 2857, 2227, 1475, 719, 669 cm^{-1}; ^{1}H NMR (360 Hz, CDCl$_3$) δ 0.88 (3H, t, $J = 6.6$ Hz), 1.15–1.44 (22H, m), 1.54 (2H, tt, $J = 7.0, 7.0$ Hz), 2.02 (1H, s), 2.29 (2H, t, $J = 7.0$ Hz); ^{13}C NMR (CDCl$_3$) δ 14.11, 19.32, 22.72, 27.96, 28.85, 29.05, 29.40, 29.47, 29.62, 29.70, 29.73, 31.96, 59.45, 61.18, 65.25, 65.73, 68.69, 80.23.

Then, by alternate repetition of evaporation of hexane and addition of tetrahydrofuran (THF), the solvent was changed from hexane to 100 cm^3 of THF. Complete evaporation of the solvent was also avoided during this procedure. To this solution were added *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (116 mg, 1 mmol) and copper(I) chloride (100 mg, 1 mmol). While it was stirred for 3 h at ambient temperature, oxygen was bubbled into the solution. After the solvent was evaporated under reduced pressure, diluted hydrochloric acid was added to the residue, and it was extracted with hexane. The hexane layer was dried with anhydrous sodium sulfate and filtered. The filtered solution was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane–benzene). The crude solid was recrystallized from the mixture of hexane and benzene to give 419 mg (39%) of 6: mp 78–79 °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,

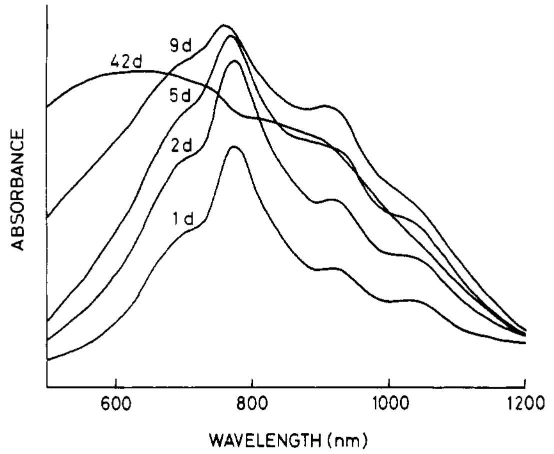

Figure 3. Visible and near IR spectral changes of THY in the course of solid-state polymerization at ambient temperature.

29.64, 31.92, 60.34, 61.46, 62.36, 62.70, 65.61, 81.91. Anal. Calcd for $C_{40}H_{56}$: C, 89.15; H, 10.85. Found: C, 88.89; H, 11.01.

Measurement of Solid-State High-Resolution ^{13}C NMR during Polymerization. The monomer sample was packed into a NMR rotor just after recrystallization. Since the monomer is light sensitive, the rotor was kept in the NMR probe during the measurement of ^{13}C NMR spectra. The ^{13}C spectra were recorded on a JEOL GSH-200 spectrometer at 50.23 MHz. Cross polarization (CP) and dipolar decoupling (DD) experiments under magic angle spinning (MAS) were performed at 24 °C. Typical acquisition parameters for the CP experiment were as follows: CP 3 ms, ^{1}H 90° pulse 4.2 μs. In both experiments the MAS speed was about 4.5 kHz. The ^{13}C shifts were referenced to the CH_2 peak of external adamantane at 29.5 ppm from tetramethylsilane.[31] In the early stage of the polymerization reaction, 200 accumulations requiring 30 min per experiment were performed. Spectra were acquired until no more changes were observed ($\sim$10 days). Dipole-dephased spectra, useful in detecting quaternary and mobile carbons and TOSS (total suppression of spinning sidebands), were acquired from time to time during this 10 day period. After the 10 day period, the ^{13}C NMR spectra were occasionally measured.

Other Spectroscopic Measurements and X-ray Diffractions during Polymerization. IR absorption spectra were measured using a JASCO IR-810. Visible and near IR absorption spectra were measured using a Shimadzu UV-3100. Absorption changes in both types of spectra during polymerization were observed in KBr-pelletized specimens of the monomer crystals. ESR spectra were obtained using a JEOL JES-RE1X ESR spectrometer. Transmitted X-ray diffraction patterns were recorded on a powder diffractometer (Philips PW-1700) using Cu Kα radiation. All the samples measured were kept at room temperature ($\sim$20 °C) and stored covered with aluminum foil.

Results and Discussion

Absorption Spectra. Although the THY monomer could be stored as long as it was dissolved in organic solvents, solid-state polymerization started spontaneously at ambient temperature immediately after recrystallization even without light or γ-ray irradiation. In the IR spectra, large changes during polymerization were observed for the peaks at 2203 and 2169 cm^{-1} corresponding to the stretching vibration of the carbon—carbon triple bonds. These peaks monotonically decreased to almost no absorption while other peaks related to the vibration of alkyl groups remained.

The color changes of the THY crystals were as follows: The colorless monomer crystals became green in the initial stage of polymerization and then gradually became black to brownish black. The visible and near IR absorption spectral changes in the course of polymerization are shown in Figure 3. At the beginning, the largest absorption maximum was observed at 776 nm together with the shoulder around 700 nm and two smaller peaks at 1028 and 917 nm. Since the peak patterns of the absorptions at 776 and 700 nm resemble those of conventional polydiacetylenes, the first step of polymerization seemed to be 1,4-addition. When the wavelengths (λ) of the largest absorption in the initial stage of polymerization of the series of alkyl-substituted conjugated acetylenes, i.e. R—(—C≡C—)$_n$—R where $n \geq 2$ and R indicates alkyl groups, are plotted, an almost linear relationship between n and λ is found, as shown in Figure 4. Though it has been already well-known that alkyl-substituted poly-yne compounds like these monomers show the absorption shift to the longer wavelength according to the number increase of the conjugated acetylenes,[32-35] a similar absorption shift is also observed for the polymers obtained from alkyl-substituted poly-ynes. This implies by analogy from polymers comprising hexatriyne and octatetrayne derivatives that the polymer structure from the dodecahexayne derivative in the first step of polymerization is a octatetrayne-substituted polydiacetylene. Absorptions in the region greater than 900 nm suggested that a more extended π-electron system rather than that of the octatetrayne-substituted polydiacetylene should be also produced. If the octatetrayne-substituted polydiacetylene is polymerized in directions other than the same column of the polymer side-chain, a three-dimensional polymer will form in the second step of the reaction, in which case such an absorption at a long wavelength should not be observed. Because the directions of the π-conjugated polymer backbones are not in the same plane and the conjugation effect is unlikely, it appears that the next polymerization step proceeds in the same column.

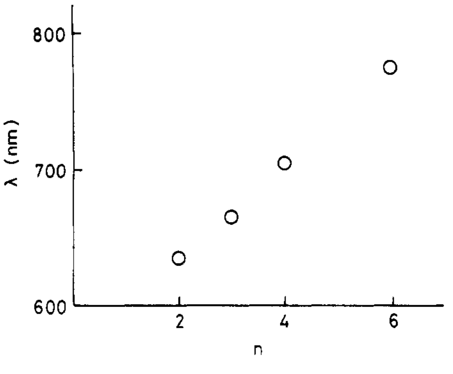

Figure 4. Relationship between the number of acetylene groups on monomers (n: R—(—C≡C—)$_n$—R, R = alkyl) and the wavelength of the largest absorption maximum at the initial stage of polymerization (λ).

Solid-State ^{13}C NMR Spectra. The CP/MAS ^{13}C NMR spectrum taken 30 min after recrystallization of THY is shown in Figure 5, and the ^{13}C chemical shift values of this spectrum together with those of the THY monomer 6 in $CDCl_3$ solution are summarized in Table 1. The assignment of the monomer solution spectrum was performed using our NMR spectral database system (SDBS-NMR).[36] The signals of the six acetylene carbons from 60.34 to 81.91 ppm in the solution spectrum indicated the monomer structure of a dodecahexayne derivative substituted symmetrically by alkyl groups. Since the spectral patterns in Figure 5 are almost the same as those of the monomer, only a small amount of polymerization had occurred in the 30 min after recrystallization. The signal at about 82 ppm is assigned to the acetylene carbons at position 15 next to the alkyl chain, which splits into two peaks with a separation of 3.3 ppm. Similarly, the signal of the acetylene carbons at position 16 splits with a smaller separation of 2.2 ppm. Although the signals of other acetylene carbons are split, they overlap in a very small

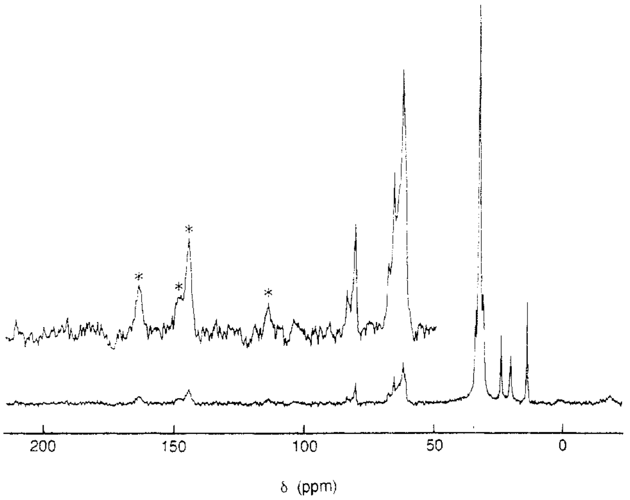

Figure 5. ^{13}C CP/MAS spectrum of THY 30 min after recrystallization. Asterisks indicate spinning sidebands. The signals can be assigned as the THY monomer.

Table 1. ^{13}C Chemical Shifts of the THY Monomer in Solution and THY in the Solid State after 30 min

solution[a] (δ_{sn})	solid state[b] (δ_{sd})	$\delta_{sd} - \delta_{sn}$	assgnt[c]
	85.2	3.3	15
81.91	81.9	0	
	69.2	3.6	16
65.61	67.0	1.4	
62.70	62–64[d]	1–2	17
62.36	d		18
61.46	d		19
60.34	d		20
31.92	35.4	3.5	3
28.82–29.64[e]	33.8[f]	4	4–12
27.83	32.5	4.7	13
22.69	25.6	2.9	2
19.52	21.8	2.3	14
14.14	15.4	1.3	1

[a] Chloroform-*d* solution. [b] CP/MAS. [c] Labeling:

$CH_3—CH_2—CH_2—(CH_2)_9—CH_2—CH_2—C{\equiv}C—C{\equiv}C—C{\equiv}C)_2—.$

1 2 3 4–12 13 14 15 16 17 18 19 20

[d] Overlapped each other. [e] Separated seven peaks for nine carbons. [f] Many peaks overlapped.

range between 62 and 64 ppm and are too complicated to be distinguished from each other. The splitting of the resonances from carbons in the same position is due to polymorphism of the monomer in the solid state. A similar ^{13}C signal splitting was found in monomers of octatetrayne derivatives containing urethane groups.[13] However it was not observed in the corresponding alkyl-substituted octatetrayne monomer of HTY (1). In the THY monomer spectrum, the ^{13}C chemical shifts in the solid state (δ_{sd}) move to the low-field side from those in solution (δ_{sn}), and these differences ($\delta_{sd} - \delta_{sn}$) are shown in Table 1. Large low-field shifts are generally observed when the packing of alkyl chains is tight. In the case of the corresponding alkyl-substituted octatetrayne derivative of HTY, a signal of the carbons originating from the mobile chains was observed as a sharp line with a ^{13}C chemical shift similar to that found in the solution spectrum.[37] Since the THY monomer did not show such mobile carbon signals, it is suggested that the stacking of the alkyl chains of the THY monomer is more rigid than in the HTY monomer.

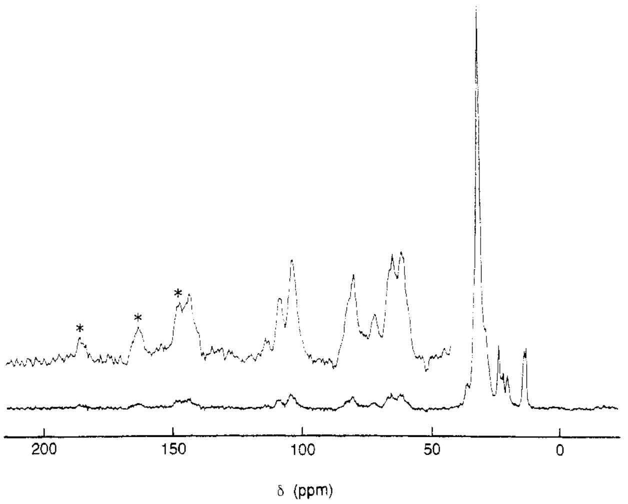

Figure 6. ^{13}C CP/MAS spectrum of THY after 22 h. Asterisks indicate spinning sidebands. The signals can be assigned as the structure 13 shown in Figure 7.

After about 3 h, additional peaks at 146, 111, and 106 ppm appeared and these intensities gradually increased. These three peaks were assigned to the unsaturated carbons in the asymmetrically-substituted polydiacetylene backbone with acetylene substituents. A ^{13}C spectrum obtained after 22 h, when those three peaks were clearly observed, is shown in Figure 6. The structure of the polymer in the first step of polymerization is presented as 13 in Figure 7. The symbols defining the carbons are given in this figure. In the spectrum in Figure 6, the peak at 73 ppm was assigned to the acetylene carbon (α) of the side chain. These assignments were based on the ^{13}C spectra of the polymer obtained from HTY.[17] Spectral changes also occurred in the alkyl carbon region. The peak at 38 ppm was assigned to the methylene carbon (14′) next to the olefin carbon in the polymer backbone. The intensity of this signal increased gradually concomitantly with the peaks for the polymer-backbone carbons. Simultaneously, the peak of the methylene carbon attached to the acetylene moiety at 22 ppm decreased its intensity, and the relative intensities of the two peaks at 22 and 38 ppm became almost the same, as shown in Figure 6. The methyl carbon signal at 15.4 ppm came to have a shoulder on the higher field side and eventually separated to form a new peak at 14.6 ppm. After 22 h, the relative intensities of these two methyl carbon peaks became almost equivalent. By this stage the main part of the crystals had changed from the monomer to 13 by the 1,4-addition. The ^{13}C chemical shifts of 13 are summarized in Table 2. together with those of polydiacetylenes with butadiynyl substituents (2) obtained from HTY. The only difference in 13 and 2 is the acetylene carbon numbers in the side chains, i.e. six for 13 and four for 2. However, the alkyl signals of 13 have a more complicated pattern than those of 2. The signal positions of alkyl carbons attached to the acetylene side chain are assumed to be near those of the monomer, and those attached directly to the backbone may move to the higher field near those of the monomer in solution. The alkyl carbons bound to the polymer backbone and the acetylene group in 2 may be in similar circumstances since the ^{13}C peaks of the alkyl chain carbons in 2 do not split.

The ^{13}C spectral pattern for both the alkyl and the unsaturated carbon signals changed continuously. The ^{13}C spectrum measured after 56 h is shown in Figure 8. The terminal methyl and methylene signals for $—CH_2—CH_3$ have become single lines, and the decreasing signals adjacent to the acetylene carbon around 22 ppm have disappeared, while the signals at about 38 ppm from the newly formed methylene groups have enlarged. At the same time, the signal intensities of the main chain acetylene and olefin carbons in the region of 100–150 ppm

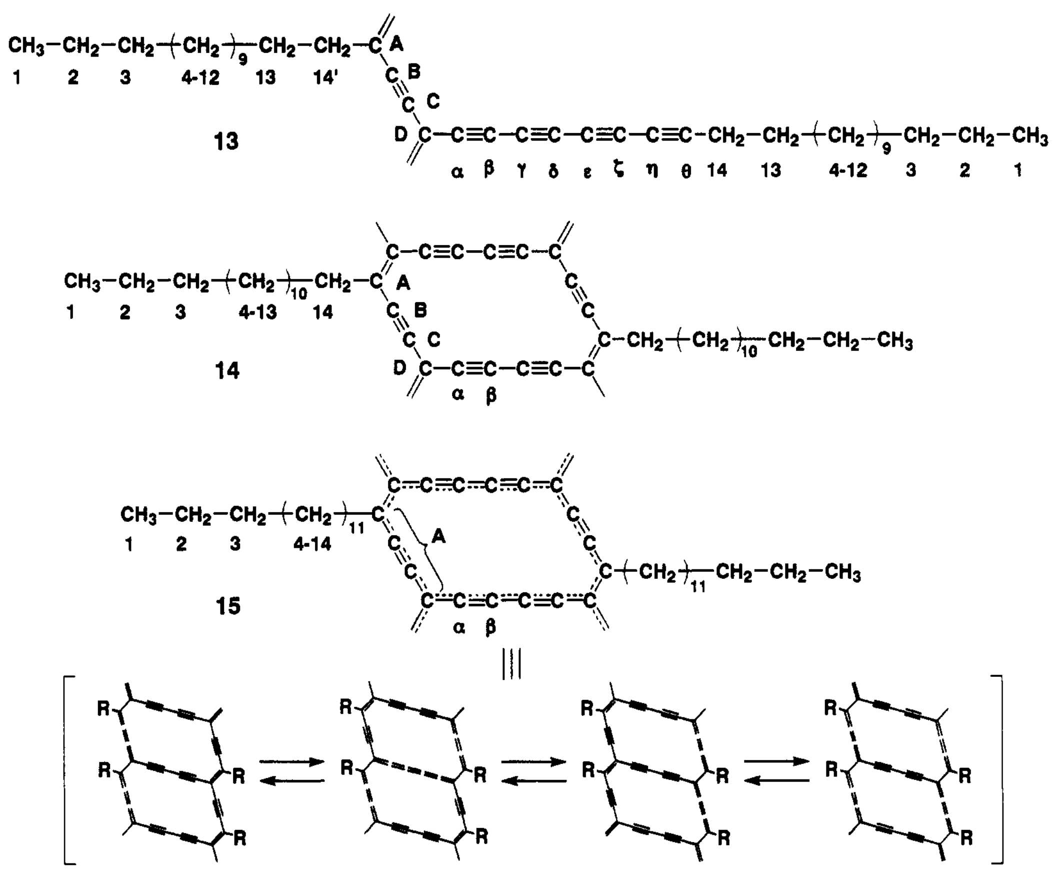

Figure 7. Proposed polymer structures from THY obtained by solid-state polymerization at ambient temperature without irradiation.

Table 2. ^{13}C Chemical Shifts (CP/MAS) of 13 from THY and 2 from HTY

13	2	assgnt[a]
146	146.3	A
111.0	110.2	D
105.7	105	B, C
84		θ
82.1	80.7	β
73.2	72.6	α
67.0		ζ
67.0		η
65		ϵ
63.6	65.4	γ
63.6	88.7	δ
37.7	37.3	14′
35.2	*b*	3
33.8[c]	33.7,[c] 31.3[c,d]	4–12
32.5	*b*	13
25.4	24.4	2
23.5		
21.9	22.3	14
15.4	14.8	1
14.6		

[a] See structure 13 in Figure 7. For the chemical structure 2, the carbons ϵ, ζ, η, and θ do not exist. The structure of the carbon θ of 13 is similar to that of the carbon δ of 2. [b] Overlapped with carbons 4–12. [c] Many peaks overlapped. [d] Mobile methylene carbons.

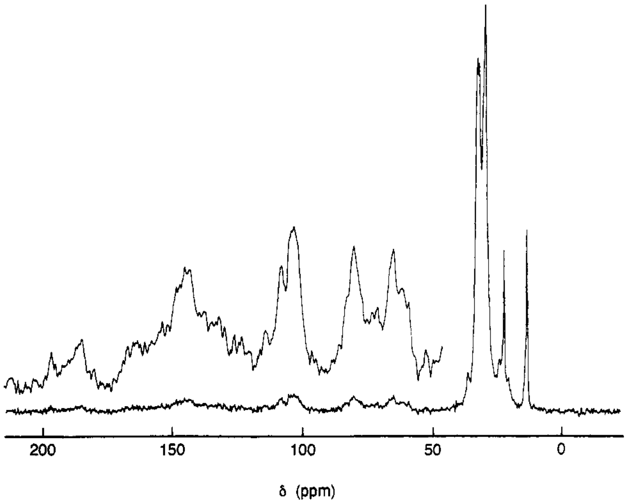

Figure 8. ^{13}C CP/MAS spectrum of THY after 56 h. The proposed structure from this spectrum is the ladder polymer 14 shown in Figure 7.

have increased relative to those of the side chain acetylene carbons (60–95 ppm), and signal patterns in the region for the unsaturated carbons became simpler than in the former spectrum in Figure 6. The spectra measured successively during these periods indicate that the second step of polymerization occurred at the ϵ- and θ-positions of 13 in the 1,4-polymerization scheme to produce a new ladder polymer (14), as presented in Figure 7 (the symbols defining the carbons are also indicated). Such a ladder-type structure with an extended π-electron system was also supported by the absorption in the greater than 900 nm region described above. The ^{13}C chemical shifts of 14 are summarized in Table 3. Since polymer 14 has a symmetrical structure, the number of inequivalent carbons in the conjugated system was expected to be five with the intensity ratio 1:1:2:1:1, which corresponds to the carbon positions A:D:B+C:β:α. The ^{13}C chemical shift values are also expected to remain similar to those of 13. Subsequently, five peaks were observed at 147, 110, 105, 82, and 67 ppm having relative intensities of 1:1:2:1:1, as shown in Figure 8. The signals at 82 and 67 ppm were assigned to the ladder carbons at the β- and α-positions of the polydiacetylene chains, respectively. The three different methylene peaks from 30 to 34 ppm were assigned to the long chain carbons 3–13 in different stacked states in the solid state. In Figure 8, broad signals were observed around 120–170 and 190 ppm, and their intensity gradually

Table 3. ^{13}C Chemical Shifts (CP/MAS) of 14

14	assgnt[a]
147	A
110	D
107	B, C
82	β
67	α
37[b]	14
33.8,[c] 30.6[c,d]	4–13
32.5	3
23.4	2
14.5	1

[a] See the chemical structure of 14 in Figure 7. [b] Broad. [c] Many peaks overlapped. [d] Mobile methylene carbons.

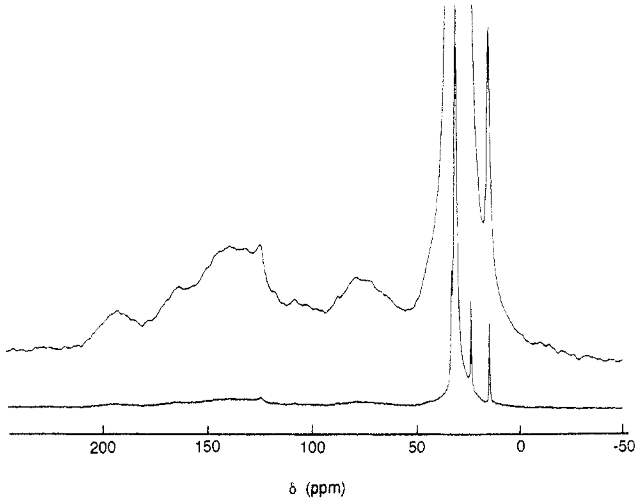

Figure 9. ^{13}C CP/MAS spectrum of THY after 11 days. The proposed structure from this spectrum is the ladder polymer 15 shown in Figure 7.

increased. The rate of spectral change slowed down at this stage.

After 11 days, the alkyl carbon signals became simpler and only four peaks were observed, as shown in Figure 9. In this spectrum, the backbone acetylene and olefin carbon signals (100–150 ppm) were observed. The integrated intensity of the ladder carbon signals between 60 and 90 ppm accounted for 30% of the signals for unsaturated carbons (60–220 ppm). Since the starting monomer of THY is a hydrocarbon and the reactions took place spontaneously in the solid state, the resulting polymer should be a hydrocarbon. No oxidation was confirmed from the IR spectra. Then the most likely chemical structures giving signals in the region above 180 ppm are allenes. We assumed that the predominant structures of the final polymer are allene-type ladder polymers 15, as shown in Figure 7. There are few ^{13}C shift data to examine for these allene structures. It has been confirmed that the solid-state ^{13}C shifts of tetraphenylbutatriene agree well with the solution data for the α and β cumulene carbons from phenyl groups, which are 124.1 and 152.9 ppm, respectively.[38] The effects of the number of double bonds have been studied in solution, and the carbons at the β-position from the substituents in the allenes having an even-number of double bonds with an odd-number of sp-carbons give peaks between 180 and 210 ppm.[39,40] From comparison with the data of 2,4-dimethyl-2,3-pentadiene and tetraphenylpropadiene, the ^{13}C chemical shift values of the α and β carbons of the methyl derivative move about 20 and 10 ppm to the lower field, respectively. Although model compounds for the proposed structure of 15 could not be found and the substituent effects to the ^{13}C chemical shifts for longer allene systems are uncertain, the ^{13}C chemical shift values observed in Figure 9 seem reasonable.

Table 4. ^{13}C Chemical Shifts (δ) and the Spin–Lattice Relaxation Time (T_1) of 15 Obtained after 6 Months from THY and Alkane

15[a]		alkane[b]		
δ	T_1 (s)	δ[c]	T_1[d] (s)	assgnt[e]
196[f]				A
165[f]				
145[f]				
130[f]				
65–80[f]				α, β
32.5	0.70	32.02	5.7	5–14[g]
30.6	0.46	29.79	4.4	3
h		29.47	5.0	4
23.3	1.1	22.78	6.6	2
14.4	2.3	14.14	8.7	1

[a] CP/MAS. [b] Chloroform-*d* solution. [c] For tetradecane from ref 32. [d] For decane from ref 37. [e] See the chemical structure of 15 in Figure 7. For alkane, the assignment numbers are the same as the position ones. [f] Very broad. [g] For tetradecane, 5–7 and for decane, 5. [h] Overlapped with carbons 5–14.

The ^{13}C NMR spectra were regularly measured over 6 months (190 days) and the polymer structure became almost stable after this period. After 6 months, the relative intensities in the unsaturated carbon region were independent of CP time. The alkyl signal positions became constant after 11 days (see Figure 9). However their line widths gradually broadened to double the width after 6 months.

The ^{13}C chemical shifts for 15 and spin–lattice relaxation times (T_1) measured after 6 months for the alkyl carbons are summarized in Table 4, together with those for alkanes in $CDCl_3$ solution,[36,41] for comparison. The signal at 30.6 ppm from the eleven methylene carbons relaxed exponentially within experimental error. The T_1 values of these carbons are extremely short, compared to the values hitherto observed for polydiacetylenes.[29,30,37] The peak positions of the alkyl carbons are nearly the same as those of the alkanes and the THY monomer in $CDCl_3$ solution. Also the methyl carbons have the longest T_1 which is similar to that measured in solution in the extreme narrowing condition. Thus the motions of the alkyl carbons of 15 have some similarity to those in the solution state, suggesting high mobility of the alkyl chains.

The ^{13}C signals around 60–90 ppm assumed to be acetylene carbons in the bridge of two conjugated backbones gradually decreased. Although the acetylene and olefin carbon signals in the ene-yne type polydiacetylene structure between 100 and 110 ppm also gradually decreased, they still remained even after 1 year. The decrease of acetylene carbons together with an increase of olefin carbons around 120–160 ppm implies the cycloaromatization[42,43] of the polymer structure 14 or 15.

ESR Spectra. Almost no ESR signals were detected just after the recrystallization of the THY monomer. The spectrum measured 4 h after recrystallization showed a single line at a *g* value of 2.0034 and had a peak-to-peak line width of 0.63 T and a spin density of 5.0×10^{15} spin/g. The ESR spectra at the initial stage of photopolymerization of a butadiyne monomer PTS (2,4-hexadiyne-1,6-diyl bis(*p*-toluenesulfonate)) have been studied,[44–48] and relevant hyperfine patterns due to correlative diradicals, dicarbenes, and so on were reported. Since the observed ESR signal for THY had a single component, the origin of the signal was considered to be different from that for PTS. The spin density change of the THY crystals during polymerization is shown in Figure 10. Although the spectral changes were drastic in the ^{13}C NMR spectra at the early stage of polymerization until the structure of 14 became

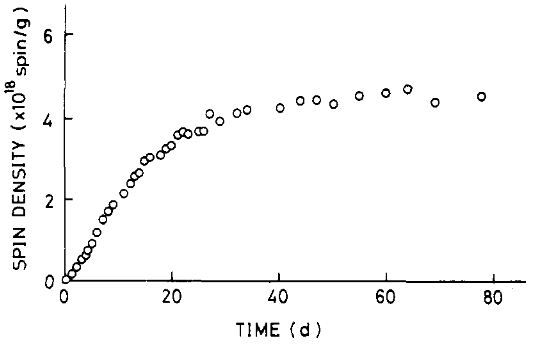

Figure 10. Increase in electron spin density of THY in the course of solid-state polymerization without irradiation at ambient temperature.

a dominant component, those in the ESR spectra were not so drastic. The ESR signal intensity increased monotonically for about 1 month and also the line width became narrower. After 1 month, the rate of increase of the spin density dropped remarkably. This corresponded to the time when almost no change was observed in the ^{13}C spectra. After 78 days, the ESR spectrum gave a single line: the *g* value, the line width, and the spin density were 2.0036, 0.41 T, and 4.6 × 10^{18} spin/g, respectively. This spin density corresponds to 240 monomer units per unpaired electron. The free radical density of the THY polymer is much larger than those of any polydiacetylenes[37] and undoped polyacetylenes.[49,50]

When we take into account that the intermediate polymer structures in the polymerization cannot exist for long before becoming the next polymer structure, the THY crystals contain some polymers having the final structure from the early stage of the polymerization. Thus, the radicals probably originate from the final polymer structure. For the polymer structures **13**–**15** proposed from the ^{13}C NMR study, there is no need to assume open shells except for terminals of the polymers. However, the very large spin densities observed in the ESR spectra are accounted for as follows. In the polymer structure of **15**, the change from one structure to another resonance structure may be accompanied by the occurrence of unpaired electrons or partial cycloaromatization of the ring structure of **14** or **15** may give a pair of radicals.

Powder X-ray Diffraction. To study the crystallinity of the polymers, changes in X-ray diffraction patterns of the powder crystals were examined from the monomer, as shown in Figure 11. For the THY monomer, several large and sharp diffraction peaks were observed around 20–24 and 28–29° in 2θ angle. The largest peak at 20° corresponds to the spacing of 0.44 nm probably due to the alkyl side-chain packing. Although these peak positions did not move during the polymerization, the peaks gradually broadened and their intensities decreased. The final polymer **15** showed no fine diffraction patterns. The broad peak of the final polymer around 20° indicated that a structural regularity remained between adjacent alkyl chains. Observation of crystals of the final polymer using an optical microscope under cross Nicol conditions indicated that most of the conjugated main chains were aligned in one direction.

In conclusion, a dialkyl-substituted dodecahexayne derivative (THY **6**) was synthesized and its solid-state polymerization was investigated. THY was found to be polymerized spontaneously at ambient temperature even without light or γ-ray irradiation. From the solid-state ^{13}C NMR spectra, the polymerization scheme proposed was as follows. In the first step of solid-state polymerization, the monomer **6** is polymerized at the 1,4-position of dodecahexayne to give a polydiacetylene substituted by alkyl and octatetraynyl groups (**13**). In the second step, the polymerization occurs at the 9,12-position of the original dodecahexayne moiety to give a ladder polymer of two polydiacetylenes bonded by butadiynylene groups (**14**). Production of such a ladder-type polymer was also supported by visible and near IR absorption spectra which showed unexpected absorption in the longer wavelength region over 900 nm. In the last step, allene structures are produced in the ladder polymer, and plausible structures are thought to be the trienes in the polydiacetylene backbones (**15**). ESR spectroscopic results revealed that the final polymer **15** has a partial open shell structure. Crystallinity was gradually lost during the polymerization, and only the regularity between adjacent alkyl chains remained in the final polymer **15**.

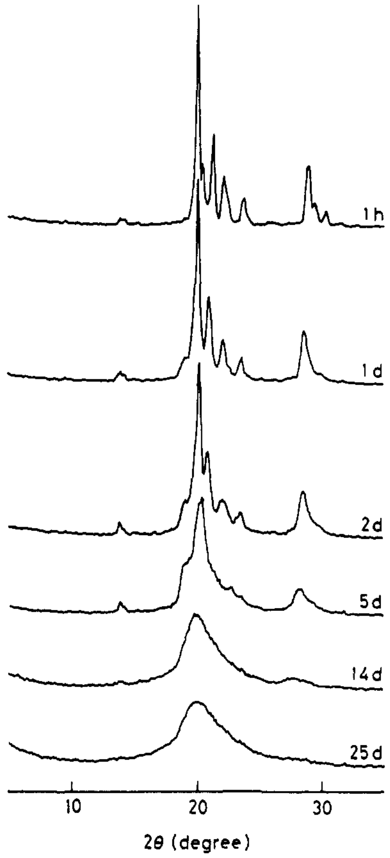

Figure 11. Changes in X-ray diffraction patterns of THY in the course of solid-state polymerization.

As was found in this study, the THY polymers exhibit the absorption shifted to a wavelength longer than that of the conventional polydiacetylenes and are expected to show interesting physical properties, i.e. nonlinear optical properties. However, in this stage, such evaluations have not succeeded because the THY polymers are insoluble, and single crystal growth and thin film fabrication of the THY monomer are also difficult. This is natural since THY was synthesized from the point of simplicity for the structural analyses of the polymer. In order to clarify physical properties of the polymers, syntheses of modified dodecahexayne derivatives with better crystallinity as well as processability for sample fabrication are currently in progress.

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