Structures of the Polymers Obtained by the Solid-State Polymerization of Diyne, Triyne, and Tetrayne with Long-Alkyl Substituents

Shuji OKADA,* Kikuko HAYAMIZU,† Hiro MATSUDA, Atsushi MASAKI, and Hachiro NAKANISHI
Research Institute for Polymers and Textiles, 1-1-4 Higashi,
Tsukuba, Ibaraki 305
† National Chemical Laboratory for Industry, 1-1-5 Higashi,
Tsukuba, Ibaraki 305
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Structures of the polymers obtained by solid-state polymerization of diyne, triyne, and tetraynes substituted by long chain alkyl groups were investigated by solid-state ^{13}C NMR spectroscopy. Assignment of all peaks in the spectra were made successfully, referring to those of the monomers and the polydiacetylenes of known structures. It was clearly shown that the backbone of these polymers has always the same structure of $\rangle C{=}C{-}C{\equiv}C{-}C{=}\langle$. This fact suggests that only 1,4-addition polymerization takes place in the similar way for the diyne, the triyne and the tetraynes, excluding many other possible addition schemes, and the tetraynes give an interesting polydiacetylene with butadiynyl substituents. This exclusive 1,4-addition can be explained in terms of topochemical control.

Conjugated polymers are interesting for their superior third-order nonlinear optical properties. Among them, polydiacetylenes were the first conjugated polymer whose third-order nonlinear optical property was reported with expectation to surpass the semiconductors.[1] To achieve enlarged third-order susceptibilities, polydiacetylenes having π-conjugations between polymer backbone and side chains might be better candidates than those with no such π-conjugations because of increased numbers of π-electrons per repeating unit.[2,3] We have succeeded in the preparation of several series of new polydiacetylenes with aromatic rings directly bound to the main chains by proper crystal engineering.[4–9] In this context, especially interesting are the polydiacetylenes with acetylenic substituents directly bound to the main chain, since we can expect perfect π-conjugation between the main chain and substituents. Recently, we have synthesized a triyne[9] and tetraynes[10] with long-alkyl substituents and confirmed their solid-state polymerizabilities. However, the structures of these polymers were not determined exactly. This paper concerns with the detailed structural analysis of the polymers by solid-state ^{13}C NMR spectroscopy and some other measurements.

Experimental

Spectroscopy and X-Ray Diffraction. IR spectra, Visible spectra, and solution ^1H NMR spectra were measured by a JASCO IR-810, a Shimadzu UV-3100S, and a Nicolet NT-360, respectively. Transmitted X-ray diffraction patterns were recorded on a powder diffractometer (Philips PW-1700) using Cu $K\alpha$ radiation.

Solid-state high resolution ^{13}C NMR spectra were obtained by use of a JEOL FX-200 at 50.10 MHz with the cross-polarization (CP)/ magic angle spinning (MAS) method. The 90° pulse for the ^{13}C resonance was 4.5 μs and the MAS speed was between 4.8 and 5.5 kHz. The CP time was changed from 1 to 10 ms to observe the relative intensities. Dipole-dephasing spectra were measured with the delayed time of 40 μs for the assignment. Also the single pulse measurement with ^1H decoupling and MAS was carried out to observed mobile carbons. The ^{13}C chemical shifts were referred to external adamantane, where the CH_2 peak was set as 29.5 ppm. Solution-state ^{13}C NMR spectra were also observed by the same spectrometer. Chloroform-*d* including a small amount of tetramethylsilane was used as a solvent.

Synthesis of Monomers. The synthetic procedures of the compounds used were shown in Fig. 1. 10,12,14-Nonacosatriynoic acid (14-3A-8C), as a triyne compound, was prepared according to the procedure described before.[9] Tetrayne compounds of 15,17,19,21-hexatriacontatetrayne (14-4A-14) and 19,21,23,25-tetratetracontatetrayne (18-4A-18) were also synthesized as described before.[10] 15,17-Dotriacontadiyne (14-DA-14) was synthesized as a reference of this series of compounds, according to the procedure described below.

14-DA-14. To a solution of *N,N,N′,N′*-tetramethylethylenediamine (580 mg, 5 mmol) and copper(I) chloride (500 mg, 5 mmol) in tetrahydrofuran (150 cm^3), 1-hexadecyne (11.1 g, 50 mmol) was added. While it was stirred for one day at ambient temperature, oxygen was bubbled into the solution. After evaporating the solvent, hydrochloric acid solution was added to the residue and the mixture was extracted with hexane. The hexane layer was dried with anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, hexane) to give 9.90 g, (90%) of 14-DA-14. After recrystallization from hexane, 3.59 g of pure 14-DA-14 was obtained. Mp 50—51 °C; IR(KBr) 2950, 2924, 2857, 2179 (weak), 2146 (weak), 1473, 1418, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (6H, t, J=6.4 Hz), 1.26 (40H, m), 1.37 (4H, m), 1.51 (4H, tt, J=7.1, 6.7 Hz), 2.24 (4H, t, J=6.7 Hz). Found: C, 86.80; H, 13.20%. Calcd for $C_{32}H_{58}$: C, 86.68; H, 13.43%.

Polymerization. Absorption spectral changes of the compounds during photopolymerization were followed using KBr-pelletized specimens under the irradiation of an 8 W UV lamp (Tokyo Kogaku Kikai K. K. PUV-1A) at the distance of 2 cm. Polymers were obtained by γ-ray induced polymerization. The doses of ^{60}Co γ-ray were 112 Mard for 14-DA-14, 57 Mrad for 14-3A-8C, 31 Mrad for 14-4A-14 and 47 Mrad for 18-4A-18, respectively, with the dose rate of ca. 0.15 Mrad h^{-1}. Since the polymers are insoluble in the organic solvents

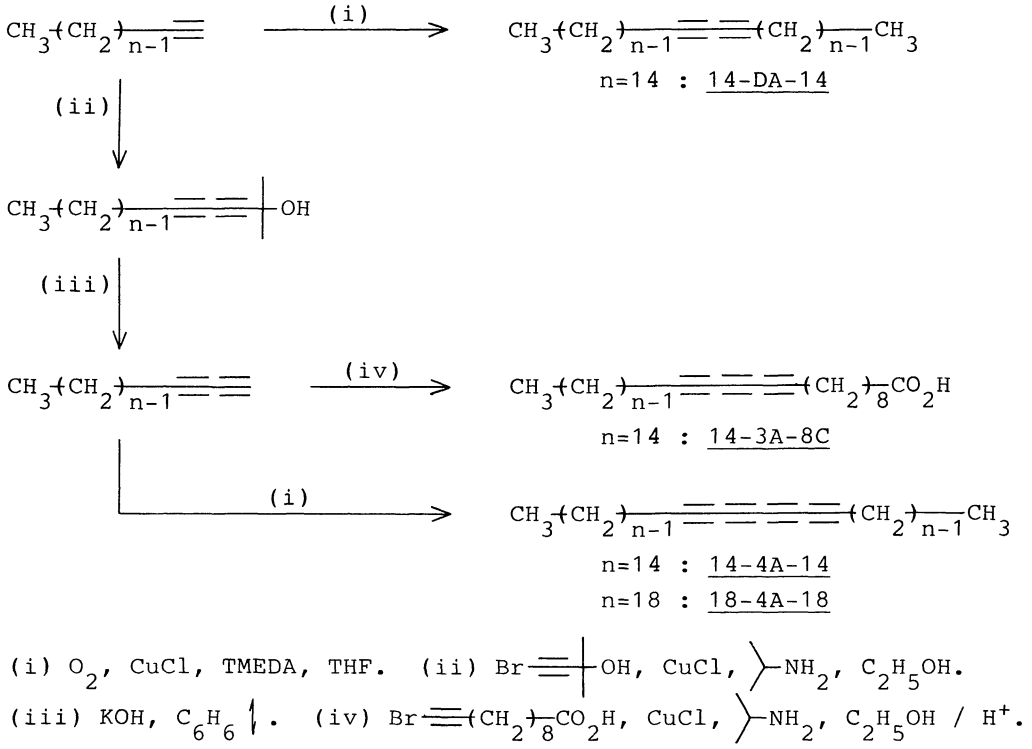


Fig. 1. Synthetic procedure of the monomers.

which can dissolve the monomers, the polymer conversion was determined gravimetrically after the solvent extraction of the monomers. Although the 14-4A-14 and 18-4A-18 were polymerized almost quantitatively, the conversion of 14-DA-14 and 14-3A-8C were 57% (after hexane extraction) and 86% (after chloroform extraction), respectively.

Results and Discussion

Visible and IR Spectra and X-Ray Diffraction. Figure 2 shows the visible absorption spectral change of 14-DA-14 during photopolymerization. The characteristic absorption maximum of polydiacetylene as a conjugated polymer was observed around 635 nm. 14-3A-8C, 14-4A-14, and 18-4A-18 were also polymerized by UV irradiation to become deep blue-colored polymers. Table 1 shows the comparison of the absorption maxima at the longest wavelength of the polymers from 14-DA-14, 14-3A-8C, 14-4A-14, and 18-4A-18. The absorption maxima of the polymers shifts to the longer wavelength as the number of acetylene units in the corresponding monomers increases. The increase of the acetylene units in the monomer brings the more extended π-conjugation and narrower band gap in the polymers synthesized by the solid-state polymerization.

IR spectra of 14-3A-8C, 14-4A-14, and 18-4A-18 monomers show a strong absorption in the stretching band region of acetylenic triple bonds. In their polymers, the stretching band becomes weaker but remains. If all the acetylene units were included in the polymer backbone, the bands should disappear because of the symmetric structure around acetylene

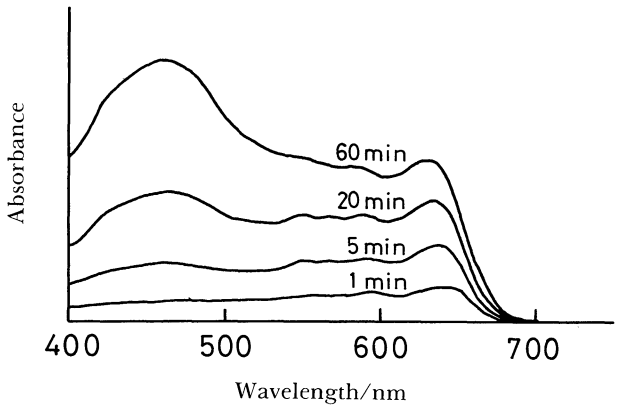


Fig. 2. Visible spectral change of 14-DA-14 depending on UV irradiation time.

Table 1. The Longest-Wavelength Absorption Maxima at the Initial Stage of Polymerization

Compound	λ_{max}/nm
14-DA-14	640—630
14-3A-8C	670—660
14-4A-14, 18-4A-18	710—700

units. Thus, one or more acetylene bonds must be in the side chains.

Crystallinity was checked by X-ray powder diffraction analysis. All the monomers showed several sharp diffraction peaks. The polymers of 14-3A-8C, 14-4A-14, and 18-4A-18, however, showed only broad peaks and the largest main peak was around 19—20°. This peak corresponds to the spacing of ca. 0.45 nm indicating that regularity between adjacent alkyl chains was maintained even in these polymers. On the contrary, the polymer of 14-DA-14 showed several sharp peaks, reflecting the high crystallinity.

^{13}C NMR Spectra. Tables 2, 3, and 4 show the ^{13}C chemical shifts of the monomers of 14-DA-14, 14-3A-8C, and 14-4A-14, respectively, in the solution and in the solid-state. The assignment was first carried out for the monomers in solution. The acetylenic carbons were assigned from ^{1}H undecoupled spectra. For instance, 14-4A-14 monomer gives the four ^{13}C peaks at 80.5, 65.7, 61.4, and 60.6 ppm, corresponding to the existence of four pairs of nonequivalent acetylenic carbons. It is known that the coupling constants of those carbons with α-methylene protons decrease with the numbers of the bonds between them. Since the coupling constants of the signals at 80.5, 65.7, 61.4, and 60.6 ppm were 5.5 Hz, 4.6 Hz, 3.7 Hz, and undetectable, respectively, the four peaks in the above order were easily identified to the four nonequivalent acetylenic carbons, i.e., from the outer most to the inner most ones in the same order. This trend is the same as the di-*t*-butyl-substituted octatetrayne.[11]

The ethynylene group causes the higher field shift of about 10 ppm to α-CH_2 but none to β- and γ-CH_2. Thus, among many carbon atoms in the alkyl chains, α-CH_2 can be identified. Though the monomer of 14-3A-8C in solution showed three pairs of acetylenic carbon peaks with small splittings because of its unsymmetrical structure, the differences were very small and less than 0.5 ppm and their assignments were straightforward as shown in Table 3. The ^{13}C spectral patterns of the monomers in chloroform-*d* solution are saved in the Spectral Database System (SDBS) constructed by National Chemical Laboratory for Industry[12].

The solid-state ^{13}C spectra of the 14-DA-14 and 14-4A-14 monomers observed by single-pulse MAS method with ^{1}H decoupling resemble to the corresponding solution-state spectra, and this suggests that these monomer contain very mobile molecules within

Table 2. ^{13}C Chemical Shifts of 14-DA-14 Monomer

Solution-state	Solid-state		Assignment[a]
	MAS	CP/MAS	
77.5	76.8 sharp	78.7 broad	6 -C≡
65.4	66.8 sharp	65.0 broad	7 -C≡
32.0	32.7	—[b]	3 CH_2
—	—	34.0	4 CH_2 stacked
29.7[c] broad	30.5	30.5	4 CH_2
		25.7	2 CH_2 rigid
22.7	23.4	23.4	2 CH_2 mobile
		22.1	5 CH_2 rigid
19.3	19.9	20.0	5 CH_2 mobile
		15.4	1 CH_3 rigid
14.1	14.6	14.7	1 CH_2 mobile

a) CH_3–CH_2–CH_2–(CH_2)$_{10}$–CH_2–C≡C–C≡C–(CH_2)$_{13}$–CH_3.
1 2 3 4 5 6 7
b) Overlapped with the carbons 4. c) Many peaks overlapped.

Table 3. ^{13}C Chemical Shifts of 14-3A-8C Monomer

Solution-state	Solid-state[a]		Assignment[b]
	MAS[c]	CP/MAS	
179.9	182.5	182.2	11 -CO_2H
79.3[d]	81 w	81.1	6 -C≡
	78 vw	78 vw	
65.7[d]	67 w	67.1	7 -C≡
	65 vw	66 vw	
60.4[d]	62 w	62.3	8 -C≡
	60 vw	60 vw	
34.0	35.7	35.6	10 CH_2
31.9	—[e]	—[e]	3 CH_2
	34.3 vs	34.3 vs	4 CH_2
28.4[f] broad	30 w	30.4 w	
24.6		26.6	9 CH_2
22.7	25.8 s	25.8	2 CH_2
19.4	22 w	21.9	5 CH_2
14.1	16.0 s	15.9	1 CH_3

a) vw: very weak, w: weak, s: strong, vs: very strong.
b) CH_3–CH_2–CH_2–(CH_2)$_{10}$–CH_2–C≡C–C≡C–C≡C–
1 2 3 4 5 6 7 8 8 7 6
CH_2–(CH_2)$_5$–CH_2–CH_2–CO_2H. c) Very intensive.
5 4 9 10 11
d) Average of two peaks. See text. e) Overlapped with the carbons 4. f) Many peaks overlapped.

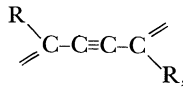
Table 4. ^{13}C Chemical Shifts of 14-4A-14 Monomer

Solution-state	Solid-state		Assignment[a]
	MAS	CP/MAS	
80.5	80.5 sharp	82 broad	6 -C≡
65.7	66.8 sharp	67 broad	7 -C≡
61.4	62.4 sharp	62 broad	8 -C≡
60.6	61.5 sharp	62 broad	9 -C≡
32.0	32.7	—[b]	3 CH_2
		33.8	4 CH_2 stacked
28.0[c] broad	30.5	30.6	4 CH_2 mobile
		25.4	2 CH_2 rigid
22.7	23.4		2 CH_2 mobile
		22	5 CH_2 rigid
19.5	20.2		5 CH_2 mobile
14.1	14.7	15.4	1 CH_3

a) CH_3–CH_2–CH_2–(CH_2)$_{10}$–CH_2–C≡C–C≡C–C≡C–C≡
1 2 3 4 5 6 7 8 9
C–(CH_2)$_{13}$–CH_3. b) Overlapped with the carbons 4.
c) Many peaks overlapped.

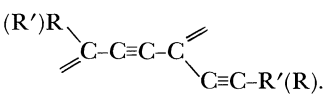
the crystals. In the CP/MAS ^{13}C spectra of these monomers, the line widths are broader and a large peak of the alkyl chain carbons in the stacked state can be observed at 33—34 ppm in addition to the mobile carbons signals at about 30 ppm. In the CP/MAS spectrum of the 14-DA-14 monomer, the signals of the mobile acetylene carbons were not observed, while the both signals of the mobile and the rigid carbons in the alkyl chains were observed as shown in Table 2. Then it is clear that the alkyl-chain carbons are more flexible than the acetylenic carbons in the 14-DA-14 monomer in the solid-state. Similarly, the CP/MAS spectrum of the 14-4A-14 monomer contains both signals of the mobile and the rigid alkyl-chain carbons, but the ratio of the mobile carbons decreases. Then the molecular motions of 14-4A-14 monomer may become slower compared with the 14-DA-14 monomer. On the other hand, the single-pulse MAS spectrum of the 14-3A-8C monomer was very intensive suggesting that the crystal structure is rigid. The reduced molecular motion in the 14-3A-8C monomer can be attributed to hydrogen bonding between carboxyl groups contained in the molecule. The magnitudes of the alkyl-chain motion of these three monomers coincide to the order of their melting points, i.e., melting points of the monomers are 50—51 °C for 14-DA-14, 58—59 °C for 14-4A-14, and 78—79 °C for 14-3A-8C, respectively. The lower melting point the monomer has, the more mobile its alkyl chain is. In 14-3A-8C, shoulders were observed in the three acetylenic carbon peaks in the MAS and CP/MAS spectra. This may be due to inhomogenious circumstances around the acetylenic carbons in 14-3A-8C monomer.

Figure 3 shows the CP/MAS ^{13}C spectra of the polymers in olefinic and acetylenic region and Table 5 lists up the chemical shifts of all the peaks. The backbone structure of 14-DA-14 polymer is



where the two acetylenic carbons and two olefinic carbons are equivalent. Actually, in Fig. 3(a), only two peaks at 101.6 and 130.2 ppm were observed. They were easily assigned to be acetylenic and olefinic carbons, respectively, which agree with those of so-far known polydiacetylenes[13–16] as summarized in Table 6.

In the polymer of 14-3A-8C, six peaks, of which two peaks around 103.9 ppm are considered to overlap because of the twice intensity, were observed (Fig. 3(b)). If they were polymerized symmetrically by 1,6-addition, the number of the peaks in this region should be three. The result clearly indicates that 14-3A-8C are polymerized unsymmetrically by 1,4-addition and therefore the backbone structure of 14-3A-8C polymer is



The same polymerization scheme was reported for a hexatriyne derivative with urethane substituents based

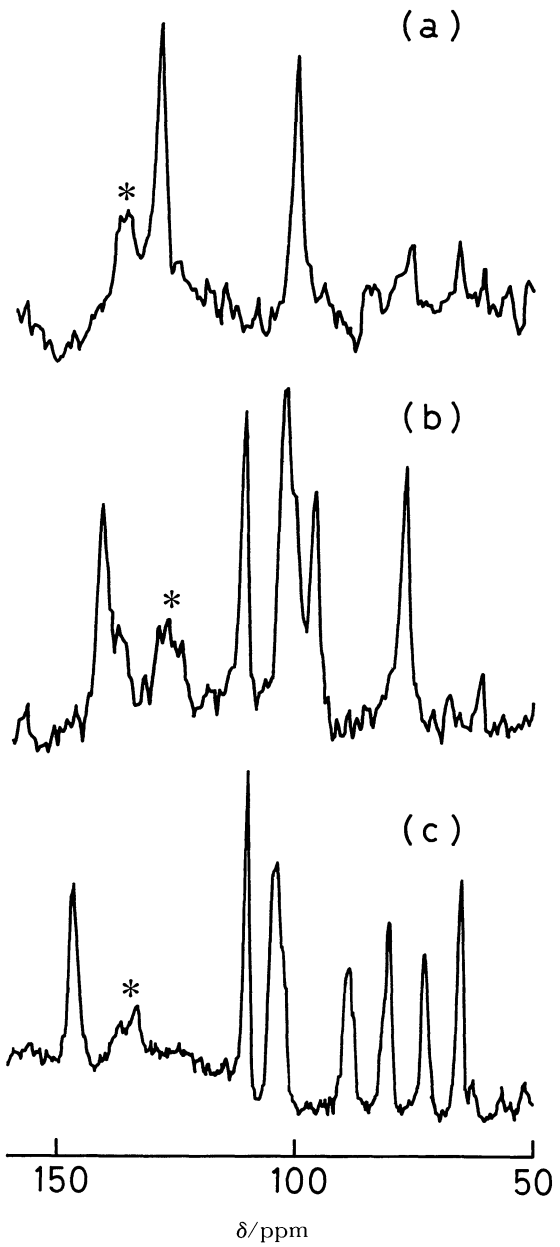
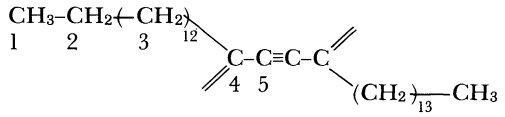


Fig. 3. ^{13}C CP/MAS spectra in the olefinic and acetylenic region of the polymers of 14-DA-14 (a), 14-3A-8C (b), and 14-4A-14 (c). Asterisks indicate background or spinning side bands.

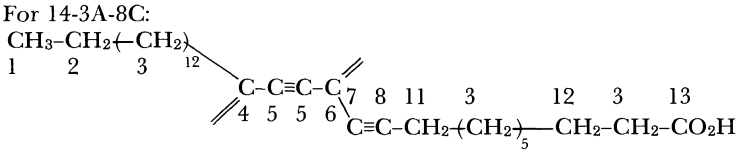
Table 5. ^{13}C Chemical Shifts (CP/MAS) of Polymers

14-DA-14	14-3A-8C	14-4A-14	18-4A-18	Assignment[a]
	181.8			13 $-CO_2H$
130.2	141.9	147.3	147.0	4 >C=
	112.0	110.3	110.5	6 >C=
101.6	103.9	105.0	104.7	5 -C≡
		89.5	89.5	10 -C≡
	97.4	80.6	80.6	8 -C≡
	77.9	72.7	72.7	7 -C≡
		65.2	65.4	9 -C≡
33.3	33.4	33.6	33.6	3 CH_2 mainly stacked
30.9				3 CH_2 mobile
	26.5			12 CH_2
23.5	24.2	24.6	24.7	2 CH_2 mobile
	21.8	22.2	22.5	11 CH_2
14.8	14.6	15.0	15.0	1 CH_3 mobile

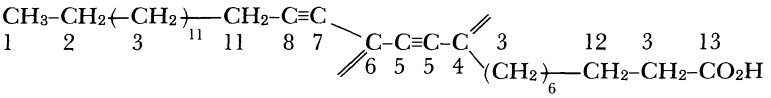
a) For 14-DA-14:



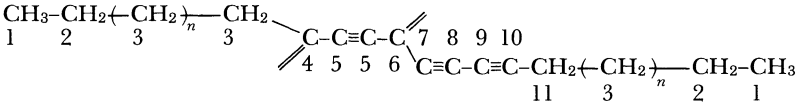
For 14-3A-8C:



or



For 14-4A-14 and 18-4A-18:

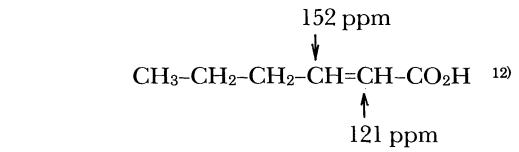


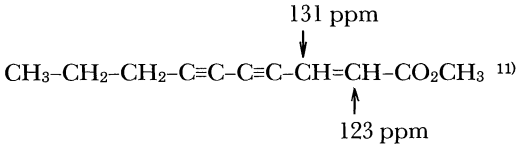
(n=11 for 14-4A-14 and n=15 for 18-4A-18)

Table 6. ^{13}C Chemical Shifts of the Backbone of Polydiacetylenes

Polydiacetylene	Measuring condition	δ/ppm		Reference
		>C=	-C≡	
4BCMU	$CDCl_3$ (30°C)	129.3	99.3	13)
PTS-12	$CDCl_3$	129	99.4	14)
DCHD	CP/MAS	129.0	104.3	15)
ETCD	CP/MAS	131.6	107.4	16)
14-DA-14	CP/MAS	130.2	101.6	This work

on the X-ray diffraction analysis.[17] The two olefinic carbons of the main chain of 14-DA-14 polymer are equivalent to give one peak at 130.2 ppm, whereas those of 14-3A-8C are not equivalent to give two peaks, i.e., one at the higher and the other at the lower field. It is known that an acetylenic group, compared with an alkyl group, attached to the olefinic moiety bring the chemical shift of the olefinic α-carbon to about 20 ppm higher field, as shows in the following example;

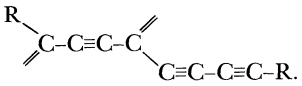




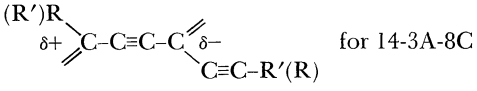
Thus, the higher field peak about 112 ppm was assigned to the olefinic carbon attached to the acetylenic side chain, and the lower field peak about 142 ppm to that attached to the simple alkyl chain. However, the splitting of the two peaks is quite large, i.e., 30 ppm for 14-3A-8C polymer whereas about 20 ppm for the typical case which is expected from the difference of the chemical shift of the two molecules shown above. This will be mentioned later again.

The peak at 103.9 ppm with larger intensity is assigned to the two backbone acetylenic carbons and is not so moved from 101.6 ppm of the acetylenic carbons of 14-DA-14. For the acetylenic side chain, the peaks at 97.4 ppm and 77.9 ppm were assigned to the β- and α-carbons from the polymer backbone, respectively, because the alkyl-attached acetylenic carbon shows the peak in the lower field as discussed in the case of the monomers.

In the same manner, the assignment of the peaks for polymers of 14-4A-14 and 18-4A-18 was performed as listed in Table 5. The spectra of 14-4A-14 and 18-4A-18 are the same except in peak intensity for the carbons of long-alkyl groups. As the chemical shifts of the three peaks in the lower field of Fig. 3(c) which correspond to the polymer backbone are similar to those of Fig. 3(b), it was estimated that 14-4A-14 and 18-4A-18 also are polymerized unsymmetrically by 1,4-addition just like 14-3A-8C. Thus, the backbone structure of 4A polymers is

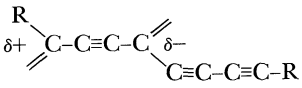


The splitting of the chemical shifts between two olefinic carbons are about 37 ppm and larger than that of 14-3A-8C. One of the plausible explanation of this splitting may be the polarization of the main chain as follows;



for 14-3A-8C

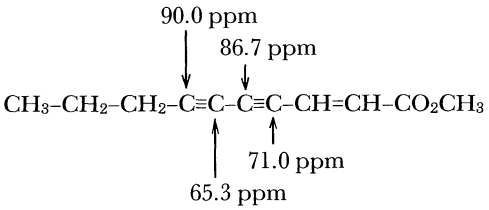
and



for 14-4A-14 and 18-4A-18,

respectively. This polarization should be enhanced in 14-4A-14 and 18-4A-18 polymers because of the more conjugated side chains.

The diacetylenic side chain was assigned by referring the following example;[11]



The peaks at about 90, 81, 72, and 65 ppm in 14-4A-14 and 18-4A-18 polymers are for the carbons at δ-, β-, α-, and γ-positions from the polymer backbone, respectively.

From these results, it has been clarified that only 1,4-polymerization occurs even in triyne and tetrayne compounds. This can be explained by so-called "topochemical control"; that is, the molecular arrangement in the crystal geometrically allows only the exclusive reaction path among many possible paths since the molecular movements are very restricted in the crystal.[18] It is known that the solid-state polymerizability of diacetylene monomers to the well-known polydiacetylene structure via 1,4-addition can be characterized by the stacking distance of the monomer array (d) and by the angle between the diacetylene rod and stacking axis (Φ).[19] And the maximal reactivity is expected for $d \approx 0.5$ nm and $\Phi \approx 45°$. When 14-4A-14 molecules are packed, using a space-filling model, without any gaps between molecules, the perpendicular distances of adjacent alkyl groups and adjacent tetraacetylenic moieties are 0.45 nm and 0.34 nm, respectively. Under this condition, d and Φ

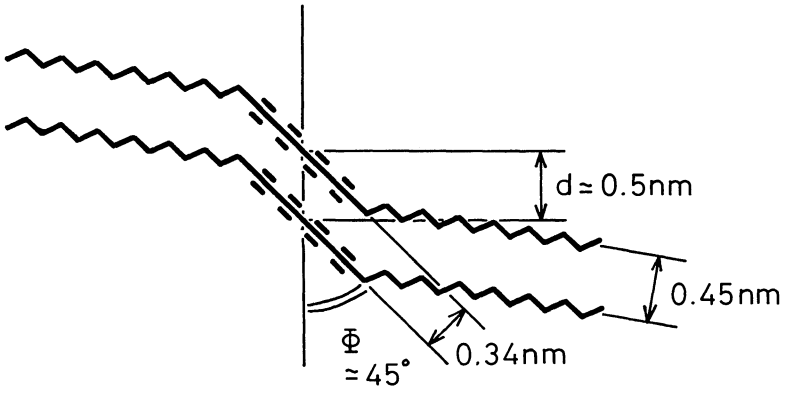


Fig. 4. Molecular packing scheme of 14-4A-14.

become ca. 0.5 nm and ca. 45°, respectively, as shown in Fig. 4. This is the case of the alkyl-substituted diynes and triynes, and the packing is exactly the best one for the 1,4-addition and not for other schemes such as 1,2-, 1,6-, and 1,8-additions.

For the tetrayne compounds, two different types of 1,4-polymerization are possible as mentioned in the previous paper,[10] i.e., the unsymmetrical polymerization as shown in this work and the symmetrical polymerization to give a di(1-alkynyl)-substituted polydiacetylene. The distance between the reacting carbons of the adjacent molecules are the same for the both polymerization procedures because tetrayne moiety stacks parallel. Only difference between two possible schemes is the existence of the reactive carbon with an alkyl chain in the case of unsymmetrical polymerization. Since the alkyl chain is more mobile than the acetylene moiety, the acetylenic carbon bound to an alkyl group can be assumed to become a starting point of the polymerization which results in the present unsymmetrical polydiacetylene structures.

In conclusion, the structures of the polymers from alkyl-substituted triyne and tetraynes were analyzed especially by solid-state ^{13}C NMR spectra. It has been found that triyne and tetraynes are polymerized unsymmetrically via 1,4-addition to give the polydiacetylene with acetylenic side chains and the polydiacetylenes with diacetylenic side chains, respectively. As the structure of the polydiacetylenes with diacetylenic side chains are confirmed, polymerization of the diacetylene moieties in side chain seems to be interesting to obtain a novel class of π-conjugated polymers and the investigation is currently in progress.

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