Synthesis and Solid-State Polymerization of ω-(1,3-Butadiynyl) Substituted 1-Alkanol and Alkanoic Acid

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(Received June 24, 1993)

ω-(1,3-Butadiynyl) substituted 1-alkanol and alkanoic acid were synthesized and their polymerization behavior in crystals and in Langmuir–Blodgett (LB) films were investigated. Polymerization, using UV or γ-ray irradiation or thermal treatment, resulted in red- or golden-colored polymers. Since the absorption edge in the visible spectra of these polymers appeared at shorter wavelengths than those of the well known blue-colored polydiacetylenes, π-conjugation is considered to be deteriorated to some extent. IR, X-ray diffraction, and solid-state ^{13}C NMR measurements showed that the polymerization does not proceed in a single-crystal-to-single-crystal transition manner via regular 1,4-addition but with deterioration of the crystalline lattice.

Polydiacetylenes have attracted much attention due to their large third order nonlinear optical properties both in crystals,[1] and in Langmuir–Blodgett (LB) films.[2] In optical device applications, LB films have the advantages that their thickness and arrangement may be controlled on a molecular scale. Several amphiphilic diacetylenes (ADAs) have already been investigated. Most ADA studies have been on ADAs with the general formula $\mathrm{H(CH_2)_mC{\equiv}C{-}C{\equiv}C(CH_2)_nCO_2H}$ (m-nC: C is a carboxylic acid) where $m=10$—16 and $n=8$ or $m=16$—18 and $n=0$.[3] There have been only two reports on ADAs with $m=0$.[4,5] In the case of the 0-nC polymer, the conjugated backbone could be formed on the outside of the molecular layer. Since the main chains of the polymer would interact with other molecules (e.g. donors and acceptors) more easily than other m-nCs ($m\neq0$), improvements of electrical and optical properties can be expected.

This paper is concerned with the synthesis of 0-nC and their precursor alcohol 0-nA (A is an alcohol, having the general formula $\mathrm{HC{\equiv}C{-}C{\equiv}C(CH_2)_nCH_2OH}$), and their polymerization behaviors in crystals and in LB films.[6]

Experimental

Spectroscopic Measurements and X-Ray Diffractions. Visible spectra were measured using a Shimadzu UV-220. IR spectra were measured using a JASCO IR-810 and a JEOL JIR-40 was used to measure the ATR-FTIR spectra of LB films. In ATR-FTIR spectra measurement, LB films were deposited onto aluminum foils and the films were pressed together with foils onto a KRS-5 plate as a reflection medium. ^{1}H NMR spectra were obtained by a Nicolet NT-360. Solid-state high resolution ^{13}C NMR spectra were obtained using a JEOL GSH-200 with the cross-polarization/magic angle spinning (CP/MAS) method. X-ray diffraction patterns were recorded on Philips PW-1700 and Rigaku 2035 diffractometers using a Cu $K\alpha$ radiation source.

Synthesis of Monomers. 22,24-Pentacosadiynoic acid (0-20C) has been synthesized from 22-tricosenoic acid, as described in the literature.[4] However it was difficult to synthesize the starting material and to change the methylene number of n in the formula of 0-nC. To solve these problems, ω-(1,3-butadiynyl) substituted 1-alkanol and alkanoic acids were synthesized using the acetylene zipper reaction,[7] i.e. **5** to **7** or **6** to **8** in Fig. 1.

Methyl 11-Bromoundecanoate 2: A solution of 11-bromoundecanoic acid **1** (100 g, 377 mmol) and concentrated sulfuric acid (1 cm^3) in 500 cm^3 of methanol was refluxed for 12 h. After removing the solvent under reduced pressure, the residue was poured into water and extracted with benzene. The benzene layer was collected and dried with anhydrous magnesium sulfate. It was filtered and benzene in the filtrate was removed under reduced pressure. The crude product was purified by distillation to give 98 g (93%) of **2**: Bp 128—130 °C/200 Pa; ^{1}H NMR (CDCl$_3$) $\delta=1.29$ (10H, m), 1.42 (2H, m), 1.62 (2H, m), 1.85 (2H, tt, $J=7.3$, 6.8 Hz), 2.30 (2H, t, $J=7.5$ Hz), 3.41 (2H, t, $J=6.8$ Hz), 3.67 (3H, s).

11-Bromo-1-undecanol 3: A solution of **2** (28.5 g, 102 mmol) in 50 cm^3 of anhydrous ether was added to a suspension of lithium aluminum hydride (3.9 g, 103 mmol) in anhydrous ether (150 cm^3) over 40 min at 0 °C. After this was stirred for 15 min, methanol was added slowly until the generation of hydrogen gas ceased, then 250 cm^3 of 1 M hydrochloric acid (1 M $=1$ mol dm^{-3}) was added. The mixture was extracted with ether. The organic layer was then dried with anhydrous magnesium sulfate and the ether was removed under reduced pressure to give 25.0 g (98%) of **3**: Mp 41.5—43 °C; ^{1}H NMR (CDCl$_3$) $\delta=1.28$ (12H, m), 1.42 (m, 2H), 1.50 (1H, s), 1.56 (2H, tt, $J=7.0$, 6.8 Hz), 1.85 (2H, tt, $J=7.1$, 6.6 Hz), 3.40 (2H, t, $J=6.8$ Hz), 3.64 (2H, t, $J=6.6$ Hz).

1-Bromo-11-(1-ethoxyethoxy)undecane 4:[8,9] A solution of **3** (24.3 g, 97 mmol), dichloroacetic acid (0.6 cm^3) and ethyl vinyl ether (120 cm^3) was stirred for 3 d at ambient temperature. Excess sodium hydrogencarbonate was added to the solution to neutralize the acid and the solution was stirred for 4 h. The solid part was removed by filtration and the solvent was removed under reduced pressure to give **4** as a colorless oil in quantitative yield: ^{1}H NMR (CDCl$_3$) $\delta=$

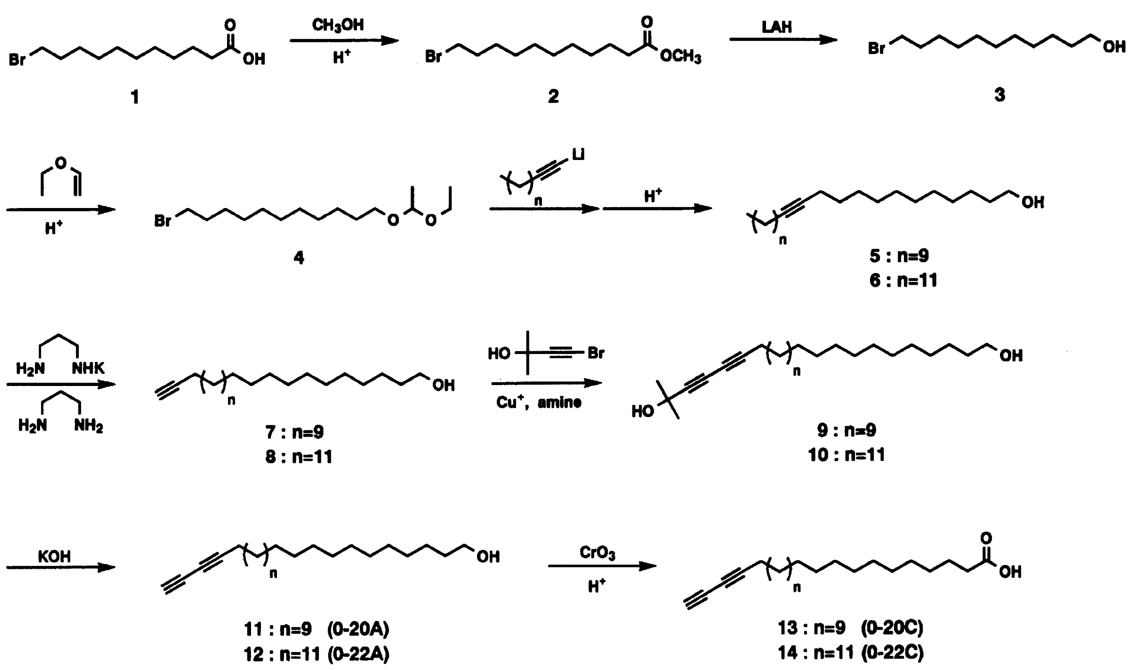

Fig. 1. Synthetic scheme of 0-*n*A and 0-*n*C.

1.21 (3H, t, J=7.0 Hz), 1.28 (12H, m), 1.30 (3H, overlapping with methylene groups), 1.42 (2H, m), 1.56 (2H, tt, J=6.9, 6.3 Hz), 1.85 (2H, tt, J=7.1, 7.1 Hz), 3.41 (3H, m), 3.48 (1H, m), 3.55 (1H, m), 3.65 (1H, m), 4.68 (1H, q, J=5.3 Hz). In the next step, **4** was used without further purification.

12-Tricosyn-1-ol 5:[9] To a solution of 1-dodecyne (14.4 g, 87 mmol) in tetrahydrofuran (THF) (50 cm^3) 1.59 M hexane solution of butyllithium (56 cm^3) was added slowly over 2 h at 0 °C under a nitrogen atmosphere. The solution was stirred for 1 h at ambient temperature and was cooled again to 0 °C. A solution of **4** (26.7 g, 83 mmol) in hexamethylphosphoric triamide (25 cm^3) was added for 2 h and the reaction mixture was stirred for 12 h at ambient temperature. Water (400 cm^3) was added and the reaction mixture was extracted with hexane. After being dried with anhydrous magnesium sulfate, hexane was removed under reduced pressure, and the residue was purified using column chromatography (silica gel, benzene) to give **5** protected with an 1-ethoxyethyl group. It was dissolved in 200 cm^3 of ethanol and 1 M hydrochloric acid (50 cm^3) was added. The mixture was stirred for 12 h at ambient temperature. The solvent was removed under reduced pressure. The residue was poured into water and extracted with hexane. After being dried with anhydrous magnesium sulfate, the solvent was removed under reduced pressure, and the residue was purified using column chromatography (silica gel, benzene) to give 11.3 g (40%) of **5**: Mp 54—54.5 °C; IR (KBr) 3371, 3284, 2959, 2923, 2850, 1463 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (3H, t, J=6.3 Hz), 1.27 (28H, m), 1.47 (4H, m), 1.57 (2H, m), 2.14 (4H, t, J=6.4 Hz), 3.64 (2H, t, J=6.6 Hz), the hydroxyl group proton was too broad to be detected. Found: C, 82.17; H, 13.03%. Calcd for $C_{23}H_{44}O$; C, 82.07; H, 13.18%.

12-Pentacosyn-1-ol 6: This synthesis was similar to that of **5** but using 1-tetradecyne instead of 1-dodecyne to give **6** in the yield of 50%: Mp 60—60.5 °C. Found: C, 82.30; H, 13.55%. Calcd for $C_{25}H_{48}O$: C, 82.35; H, 13.27%.

22-Tricosyn-1-ol 7:[7,9] Potassium hydride (6.72 g, 168 mmol) dispersed in mineral oil was washed with hexane twice under a nitrogen atmosphere. After the hexane was removed, 200 cm^3 of anhydrous 1,3-diaminopropane was added, and the suspension was stirred for 3 h at ambient temperature. 9.41 g (28 mmol) of **5** in THF (20 cm^3) was added to the solution for 1 h. After this was stirred for 3 h, 300 cm^3 of ice water was added and the mixture was cooled. The mixture was filtered and the precipitates were dried. The filtrate was extracted with benzene. After being dried with anhydrous magnesium sulfate, benzene was removed under reduced pressure. The residue and dried precipitates were gathered and purified by column chromatography (silica gel, chloroform) to give 7.01 g (74%) of **7**: Mp 74.5—76.5 °C; IR (KBr) 3367, 3289, 2915, 2849, 2110, 1473, 1462, 1064, 725, 720, 629 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.25 (34H, m), 1.54 (4H, m), 1.97 (1H, t, J=2.5 Hz), 2.18 (2H, dt, J=2.5, 7.0 Hz), 3.64 (2H, t, J=6.6 Hz), the hydroxyl group proton was too broad to be detected. Found: C, 81.99; H, 13.48%. Calcd for $C_{23}H_{44}O$: C, 82.07; H, 13.18%.

24-Pentacosyn-1-ol 8: A similar procedure to the synthesis of **7** was done but using **6** instead of **5** to give **8** in the yield of 76%: Mp 76—78 °C. Found: C, 82.25; H, 13.42%. Calcd for $C_{25}H_{48}O$: C, 82.35; H, 13.27%.

26-Methyl-22,24-heptacosadiyn-1,26-diol 9:[10,11] To a solution of **7** (1.01 g, 3 mmol) in ethanol (30 cm^3), 150 mg of copper(I) chloride and 30 cm^3 of 2-aminopropane were added at ambient temperature under a nitrogen atmosphere. After this was stirred for 10 min, 1.96 g (12 mmol) of 4-bromo-2-methyl-3-butyn-2-ol was added dropwise for 3 h. When the solution became blue upon the addition of 4-bromo-2-methyl-3-butyn-2-ol, a sufficient amount of hydroxylamine hydrochoride was added until the solution became yellow. The reaction mixture was further stirred for 1 h after addition of 4-bromo-2-methyl-3-butyn-2-ol was completed. The solvent was removed under reduced pressure and the residue was purified with column chromatography (silica gel, chloroform) to give 602 mg (48%) of **9**: Mp 81.5—82.5 °C; IR (KBr) 3401, 3247, 2985, 2915, 2849, 1471, 1172, 1159, 1056, 962, 717 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.25 (34H, m), 1.52 (6H, s), 1.54 (4H, m, overlapping to methyl groups), 2.27 (2H, t, J=7.0 Hz), 3.64 (2H, t, J=6.6 Hz), the hydroxyl group protons were too broad to be detected. Found: C, 80.33; H, 12.16%. Calcd for $C_{28}H_{50}O_2$: C, 80.32; H, 12.04%.

28-Methyl-24,26-nonacosadiyn-1,28-diol 10: A similar procedure to the synthesis of **9** was done but using **8** instead of **7** to give **10** in the yield of 46%: Mp 86—87 °C. Found: C, 80.58; H, 12.40%. Calcd for $C_{30}H_{54}O_2$: C, 80.65; H, 12.18%.

22,24-Pentacosadiyn-1-ol 11 (0-20A):[12] To a solution of **9** (500 mg, 1.2 mmol) in benzene (100 cm^3) powdered potassium hydroxide (150 mg) was added. Refluxing was continued until the disappearance of the starting material **9**, monitored by thin layer chromatography (silica gel, chloroform). The typical reaction time was from 15 min to 1 h. Then the solid part was filtered out. From the filtrate the solvent was removed under reduced pressure and the residue was purified using column chromatography (silica gel, chloroform) to give 420 mg (97%) of **11**: Mp 74.5—76.5 °C; IR (KBr) 3436, 3367, 3279, 2915, 2849, 2315, 2222, 1473, 1064, 719, 623 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.26 (34H, m), 1.53 (4H, m), 1.96 (1H, s), 2.26 (2H, t, J=7.0 Hz), 3.64 (2H, t, J=6.6 Hz), the hydroxyl group proton was too broad to be detected. Found: C, 83.47; H, 12.17%. Calcd for $C_{25}H_{44}O$: C, 83.27; H, 12.30%. In this experiment, excess time of refluxing often resulted in production of an isomer of **11** with a different position of acetylenes.

24,26-Heptacosadiyn-1-ol 12 (0-22A): A similar procedure to the synthesis of **11** was done but using **10** instead of **9** to give **12** in the yield of 95%: Mp 77.5—79 °C. Found: C, 83.76; H, 12.42%. Calcd for $C_{27}H_{48}O$: C, 83.44; H, 12.45%.

22,24-Pentacosadiynoic Acid 13 (0-20C):[13] To a solution of **11** (360 mg, 1 mmol) in acetone (100 cm^3) Jones reagent[14] was added at 0 °C. At first the color of the solution became dark green. Addition was continued until the solution color became greenish orange. Finally 2-propanol was added to quench the activity of the excess chromium(VI) in Jones reagent until the color of the solution returned to dark green. The solution was poured into water and extracted with chloroform. After being dried with anhydrous magnesium sulfate, the solvent in the extracted organic layer was removed under reduced pressure. The residue was purified with column chromatography (silica gel, chloroform) to give 325 mg (87%) of **13**: Mp 87.5—89.5 °C; IR (KBr) 3279, 2915, 2849, 2315, 2222, 1698, 1468, 926, 720, 629 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.26 (32H, m), 1.53 (2H, tt, J=7.1, 7.0 Hz), 1.63 (2H, tt, J=7.5, 7.3 Hz), 1.96 (1H, s), 2.25 (2H, t, J=7.0 Hz), 2.35 (2H, t, J=7.5 Hz), the carboxylic group proton was too broad to be detected. Found: C, 80.01; H, 11.29%. Calcd for $C_{25}H_{42}O_2$: C, 80.16; H, 11.30%.

24,26-Heptacosadiynoic Acid 14 (0-22C): A similar procedure to the synthesis of **13** was done but using **12** instead of **11** to give **14** in the yield of 85%: Mp 90—92 °C. Found: C, 80.30; H, 11.61%. Calcd for $C_{27}H_{46}O_2$: C, 80.54; H, 11.51%.

Preparation of Monolayers and Multilayers. A filmbalance (MGW Lauda) was used to measure F–A isotherms and to prepare multilayers. Monolayers were spread from chloroform solution (about 1×10^{-3} M) onto pure water for alcohols and onto 1×10^{-3} M $CdCl_2$ aqueous solution (pH 5.8) for carboxylic acid at 20 °C. They were transferred onto hydrophilic glass plates or those with a several layers of cadmium arachidate, i.e. hydrophobic plates, by LB technique under a surface pressure of 20 mN m^{-1}. A Lauda film lift FL-1 was used as a substrate lifter. The lifting and dipping rates were 4 and 6 mm min^{-1}, respectively.

Polymerization. Photopolymerization was stimulated by UV irradiation. Samples were irradiated by an 8W UV lamp (Tokyo Kogaku Kikai K.K., PUV-1A) at a distance of 2 cm. Thermal polymerization was done in the temperature-controlled oven (Yamato DN-41) at 60 °C except for the solid-state NMR experiment. In that case, a monomer was packed in an NMR rotor and after measuring the spectrum of the monomer, the sample was heated at 40 °C for 48 h in the NMR probe and the polymer spectrum was obtained. In the case of polymerization with γ-rays from ^{60}Co, the crystals were sealed in glass tubes under reduced pressure. The dose rate was about 0.15 Mrad h^{-1}. Samples for spectroscopic studies of crystals during polymerization were KBr-pelletized disks of the diacetylene microcrystals. LB films were polymerized on substrates.

Results and Discussion

0-*n*A and C in Crystals. Upon UV irradiation crystals of both 0-*n*A and C (n=20, 22) became red-colored polymers. The changes in visible spectra of 0-20A and C upon UV irradiation are shown in Fig. 2. The same spectral changes were also observed in the n=22 compounds. The color changes of 0-*n*A and C were different from those of the previously investigated amphiphilic diacetylenes, e.g. 14-8C and 18-0C which become blue polymers. However it is certain that the conjugated backbones of 0-*n*A and C are also extended because of the absorbance increase in the visible region. The color difference between 0-*n*A and C polymers and the 14-8C polymer would be the results of the conjugation length and/or structural differences in the polymer backbone.

In IR spectra, both monomers of 0-*n*A and C show two absorption bands corresponding to $\nu_{C\equiv C}$ at 2315 and 2222 cm^{-1}, and the band at 2315 cm^{-1} was weaker than the band at 2222 cm^{-1} (e.g. 0-20A in Fig. 3 (a)). However, in the polymers, those two bands almost disappeared (Fig. 3 (b)). At the same time, the bands at 3279 and 625 cm^{-1}, corresponding to $\nu_{\equiv CH}$ and $\delta_{\equiv CH}$, respectively, also disappeared. No clear new bands related to the carbon–carbon triple bonds were observed. The conversion in photopolymerization of 0-20A and C were investigated by observing the decrease of the two IR bands of $\nu_{C\equiv C}$. Figure 4 shows the relationship between UV irradiation time and monomer conversion. The conversion C_m was calculated by,

$$C_m(\%) = 100(1 - I(t)/I(0)) \qquad (1)$$

where $I(0)$ and $I(t)$ are the absorbance of the monomer and at time t after UV irradiation, respectively. The

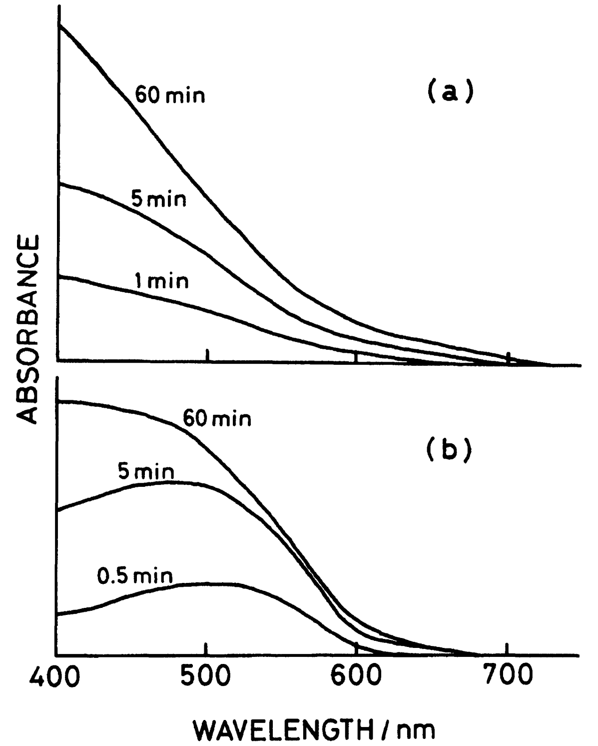

Fig. 2. Absorption spectral changes of crystals of 0-20A (a) and 0-20C (b) during UV irradiation.

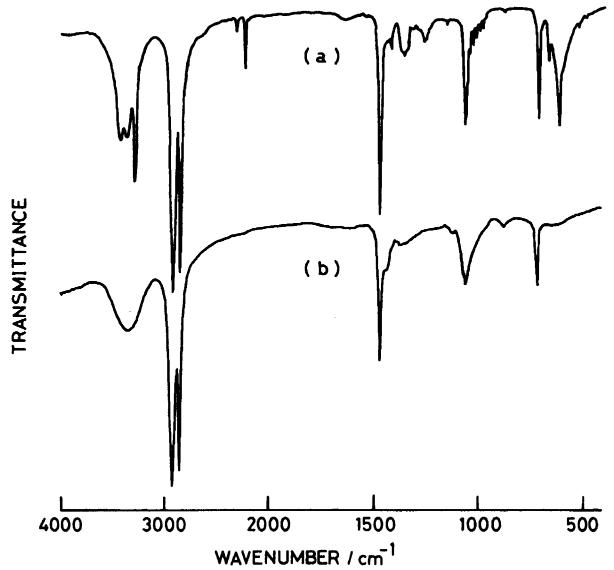

Fig. 3. IR spectra of crystals of 0-20A monomer (a) and its polymer (b).

conversions calculated from two bands agreed within experimental error. Thus, it appears that the two triple bonds of the diacetylene moiety reacted simultaneously. Conversions of both compounds were become saturated around 55%. This is because the samples were colored in the course of polymerization and the UV light gradually could not pass through the samples resulting in unreacted monomers remaining.

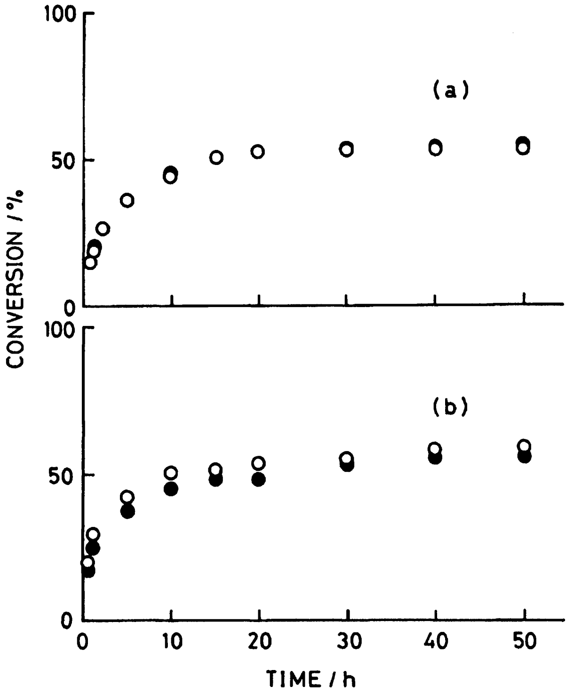

Fig. 4. Time-conversion curves in photopolymerization of crystals of 0-20A (a) and 0-20C (b), calculated from bands at 2315 cm^{-1} (○) and 2222 cm^{-1} (●), respectively.

Upon γ-ray irradiation, both alcohols and carboxylic acids became golden colored polymers. Polymer yields, calculated from the weight of the chloroform insoluble part, were 98% for 0-20A at a dose of 19 Mrad and 100% for 0-20C at a does of 92 Mrad, respectively. Since the polymer yield of 0-20C at a dose of 30 Mrad was only 32%, the polymerizability of 0-20A was higher than that of 0-20C. To check the crystallinity of these polymers, powder X-ray diffraction analysis was done on both monomers and polymers. The monomers of 0-20A and C showed several diffraction peaks between 17° and 27° in diffraction angle 2θ. However, both polymers showed a broad peak at 21.5°, corresponding to a spacing of about 0.41 nm. This indicates that some disordering occurred during solid-state polymerization, and the polymers would have structural regularities only between adjacent alkyl chains. Thus, X-ray crystallographic structure analysis was impossible. Since the diffraction intensity of 0-20C polymer was weaker than that of 0-20A polymer, it is thought that the monomer alignment of 0-20C was less suitable to be polymerized and the crystallinity of 0-20C was mostly lost during polymerization, resulting in the lower polymerizability of 0-20C.

Those alcohols and carboxylic acids were also polymerized by thermal treatment. Figure 5 shows the time-conversion curves obtained from the IR spectra. The final conversions of both compounds became nearly 100%.

Since solid-state ^{13}C NMR spectroscopy is a powerful tool for the structure analysis of the polymer in

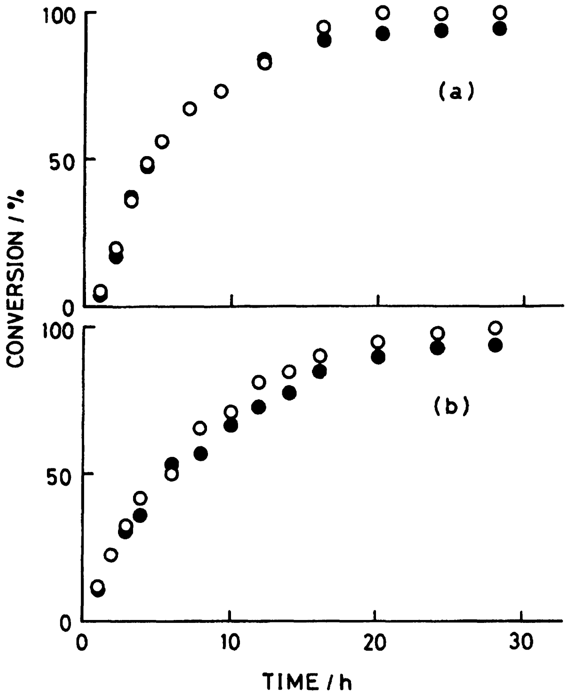

Fig. 5. Time-conversion curves in thermal polymerization of crystals of 0-20A (a) and 0-20C (b), calculated from bands at 2315 cm^{-1} (○) and 2222 cm^{-1} (●), respectively.

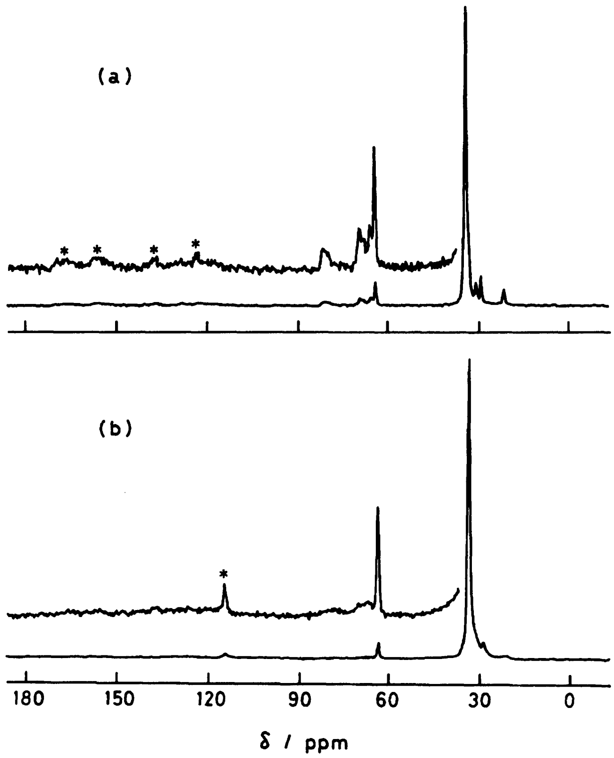

Fig. 6. The ^{13}C NMR spectrum (CP/MAS) of the 0-22A monomer (a) and polymer (b). Asterisks indicate background or spinning side bands.

Table 1. ^{13}C Chemical Shifts of 0-22A Monomer

Solution-state	Solid-state	Assignment[a)]
78.6	81	9 $-C\equiv$
66.4	69	10 $-C\equiv$
64.6	68	11 $-C\equiv$
64.3	65	12 $H-C\equiv$
63.1	64	1 $-CH_2-OH$
32.8	—[b)]	2 $-CH_2-$
29.7[c)] broad	34[c)]	5 $(CH_2)_{15}$
29.4	—[b)]	5 $-CH_2-$
29.1	—[b)]	4 $-CH_2-$
28.8	—[b)]	6 $-CH_2-$
28.0	31	7 $-CH_2-$
25.7	29	3 $-CH_2-$
19.0	21	8 $-CH_2-C\equiv$

a) $HO-\underset{1}{C}H_2-\underset{2}{C}H_2-\underset{3}{C}H_2-\underset{4}{C}H_2(\underset{5}{C}H_2)_{16}\underset{6}{C}H_2-\underset{7}{C}H_2-\underset{8}{C}H_2-\underset{9}{C}\equiv\underset{10}{C}-\underset{11}{C}\equiv\underset{12}{C}H$. b) Overlapped with the peak at 34 ppm. c) Many peaks overlapped.

solid state, the structural change of 0-22A during polymerization was monitored by ^{13}C NMR spectra under CP/MAS conditions. Figures 6 (a) and (b) show the ^{13}C CP/MAS spectra of the monomer and the polymer. The monomer peaks in chloroform-*d* solution and in solid state were assigned as summarized in Table 1. The large lower-field shifts of about 2—4 ppm in solid state compared with in solution indicates comparatively tight packing of the molecules. However, since the peak for the stacked methylenes shifted from 34 to 33 ppm during thermal polymerization, it was found that the packing of the molecules became loose. These results were also supported by the X-ray powder diffraction experiment described above.

The acetylenic peaks gradually decreased and broadened during polymerization. In the case of symmetrically-substituted and topochemically polymerized polydiacetylenes, two characteristic ^{13}C peaks appears around about 100—107 and 130 ppm, corresponding to the olefinic and acetylenic carbons of the polydiacetylene backbone.[15—17)] Thus, unsymmetrically-substituted polydiacetylenes, which were expected to be prepared from mono-substituted diacetylenes, should show four unequivalent ^{13}C peaks for the polymer backbone carbons. However, no clear peaks corresponding to the backbone appeared and even the peaks of the acetylenic carbons of the monomer almost disappeared. The remaining small broad peaks of acetylenic carbons and the methylene carbon attached to the diacetylene moiety in the spectrum of Fig. 6 (b) showed that there were unreacted acetylene parts. These were not due to the remaining monomer because no monomer was extracted by chloroform from the thermally-polymerized polymer.

From all of the analytical data, we estimated the polymer structure of 0-*n*A and C as follows. Since two $\nu_{C\equiv C}$ bands disappeared simultaneously in IR spectra, two triple bonds were reacted at the same time, indicating that 1,4-addition was the main reaction. However, other experimental results, such as no sharp excitonic absorption in the polymer visible spectra, deterioration of polymer crystallinity, and no sharp ^{13}C peaks corresponding to the carbons in the polymer backbone, showed that disorder in the polymer structures is much larger than that of the red phase of conventional polydiacetylenes. Existence of unreacted acetylene parts observed by ^{13}C NMR, in spite of no monomer, was probably due to 1,2- or 3,4-addition polymerization proceeding to a small extent. Large disorder of the polymer structure and polymerization scheme except 1,4-addition implied that polymerization proceeded not only in the same column in one direction but also partially in the other directions. The reason why the stereo-regulated 1,4-addition did not occurred in 0-*n*A and C was considered as follows. The imbalance in bulkiness of two substituents attached to the butadiynylene group, i.e. a small group of hydrogens and a rather larger group of alkyl chains, caused a large mismatch of the crystal lattice between monomers and polymers, and disorder in crystal structure increased during polymerization procedure. Such disordering may make other polymerization schemes such as 1,2- and 3,4-addition possible.

When the crystals of 0-20A were irradiated by UV in air for a long time, a small amount of carbonyl groups was detected by IR spectra, indicating that photochemical oxidation occurred. The reason why this compound was easily oxidized is thought to be that the conjugated backbones of the polymer from 0-20A were formed on the outside of the molecular layer in crystals and the polymer main chains could react with oxygen in air to give carbonyl groups. In addition, when the polymer crystals were exposed to iodine vapor, the electrical conductivity changed from the insulator range to 10^{-7}—10^{-6} S cm^{-1}. This is in considerable contrast with the previous results on poly-PTS and poly-DCHD. It is known that iodine-doping of such polydiacetylenes is impossible since the bulky substituents in a perfect and rigid crystalline lattice prevent dopants from immersing into and interacting with the polymer backbone.[18] Thus, the easy dopability of these polymers can be done with the half-naked π-conjugation in layered structures and deteriorated crystallinity.

0-*n*A and C in LB Films. Figure 7 shows the F–A isotherms of 0-*n*A and C. The limiting surface area per molecule of 0-*n*A and C were about 0.22 and 0.24 nm^2, respectively, indicating the formation of well-condensed monolayers on subphases. It seems that the surface areas of these derivatives are mainly controlled by the bulkiness of hydrophilic ends. 0-*n*A could be deposited into Y-type films on the hydrophobic substrates at a surface pressure of 20 mN m^{-1}. On the other hand 0-*n*C could be deposited into Z-type films on the hydrophilic substrates, and with further deposition, they have a tendency to be deposited into incomplete Y-type films the down stroke transfer ratio of which was less than 0.5. Since fatty acids is known to form Y-type multilayers even when X- or Z-type depositions of these compounds were done, interlayer spacings of 0-*n*C multilayers were examined by X-ray diffraction analysis. The spacings of multilayers of 0-20C and 0-22C with cadmium salts were found to be 6.00 and 6.55 nm for monomers and 6.10 and 6.61 nm for polymers, respectively. These values are only acceptable as those of Y-type multilayers. Thus, it is clear that their layer structures were changed from the Z-type of deposition into stable Y-type during the deposition procedure. The monomer spacing of 0-22C is larger than that of highly polymerizable 14-8C of 6.07 nm,[19] which has the same total carbon chain length, suggesting that the tilt angle with respect to the perpendicular direction to the substrate of 0-22C molecules in multilayers was smaller than that of 14-8C. Since the diacetylene group of 0-22C was at the hydrophobic end, the methylene chain could be packed well and the packing effect made 0-22C in multilayers rise up. Increase of the interlayer spacings after polymerization were 0.06—0.10 nm, and these values were similar to that of 14-8C of 0.12 nm.[19]

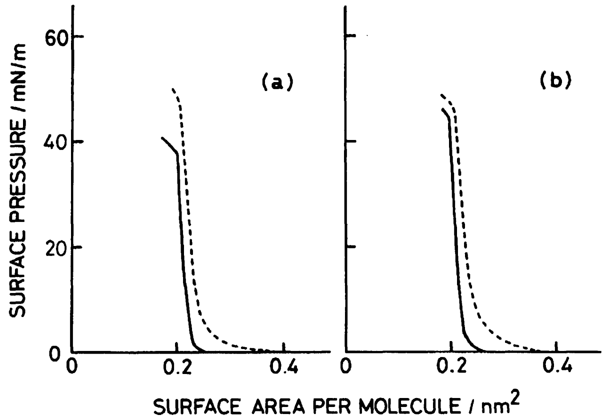

Fig. 7. F–A isotherms of 0-*n*A and 0-*n*C. (a) is for n=20 and (b) is for n=22. Solid lines are for alcohols (0-*n*A) and dotted lines are for carboxylic acids (0-*n*C).

Upon UV irradiation multilayers of 0-20A and C showed similar increases of absorbance to those of crystals in wavelengths shorter than 650 nm (Fig. 8), indicating that they are polymerized just like in crystals. However, further UV irradiation made the absorption edges of films shift to shorter wavelengths due to undulation or decomposition of the polymer backbone. In the ATR-FTIR spectra, though the absorption band of C≡C at 2315 cm^{-1} was overlapped with the absorption of carbon dioxide and was not detected, the bands at 3276 cm^{-1} for $\nu_{\equiv \mathrm{CH}}$ and 2222 cm^{-1} for $\nu_{\mathrm{C}\equiv\mathrm{C}}$ decreased with increasing time of UV irradiation but did not disappear even after 15 min of irradiation. (Fig. 9). Upon γ-ray irradiation of 0-20A LB films, those two bands almost disappeared. Since the visible and IR spectral changes of those compounds in LB films were similar to those in crystals, the polymerization of these com-

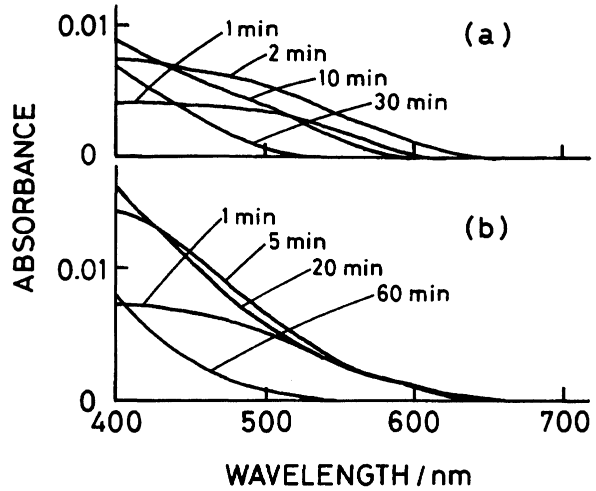

Fig. 8. Absorption spectral changes of 20 layers of 0-20A (a) and 0-20C (b) during UV irradiation.

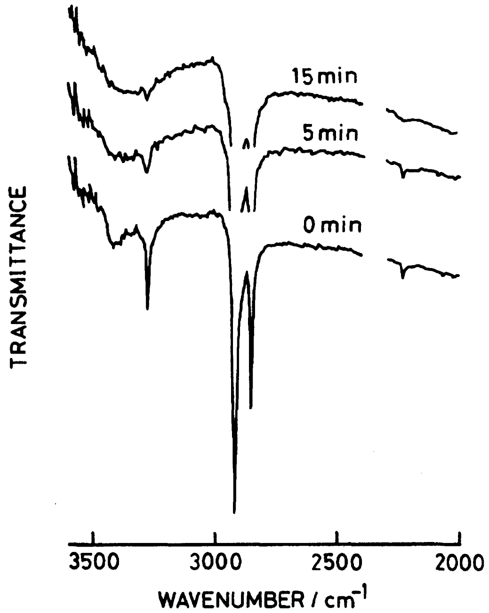

Fig. 9. ATR-FTIR spectral change in photopolymerization of 30 layers of 0-20A.

pounds in LB films is estimated to proceed in the same manner as that in crystals mentioned above. Though the multilayer of 0-20C cadmium salt has been reported to be photopolymerized at 24,25-position, i.e. the acetylene group at the end, to give polyacetylene structure substituted by 1-alkynyl groups with carboxylate at the end,$^{5)}$ such structure was not found to be a major one from our investigation.

In conclusion, ω-butadiynyl amphiphilic diacetylene derivatives in both crystals and LB films were polymerized by UV or γ-ray irradiation or heating. However, the polymerization scheme is not conventional stereoregulated 1,4-addition, but disordered 1,4-addition with a small extent of 1,2- or 3,4-additions. Though the pure mono-substituted diacetylene structure could not be realized in these compounds, it was found the polymers from 0-nA and C can interact with other molecules because of the outer position of π-conjugation in the layered structure of these polymers and deterioration of crystallinity.

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