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Synthesis and Solid-State Polymerization of ω-(4-Aryl-1,3-butadiynyl) Substituted 1-Alkanol and Alkanoic Acid

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The amphiphilic diacetylenes with directly-bound aromatic substituents, i. e. 27-aryl-24,26-heptacosadiyn-1-ols and -diynoic acids, were synthesized and the solid-state polymerization of these compounds upon γ-ray and UV irradiation was investigated. More than half of the compounds synthesized are polymerizable because the packing effect of the methylene chains makes the diacetylene moieties align into polymerizable stack. It is found that the bulkiness of hydrophilic and hydrophobic ends was an impotant factor for the polymerizability of this series of compounds.

Polydiacetylenes, which can be obtained as peculiar single crystals of conjugated polymers by the solid-state polymerization of diacetylene monomers, have caught increasing interest for third-order nonlinear optical materials.[1,2] In order to achieve higher third-order susceptibilities of polydiacetylenes, the enlarged polarization along and/or cross the π-conjugated polymer backbone is considered to be necessary. One candidate of the monomers for such polydiacetylene structure must be aryl-substituted diacetylenes. Though simple diaryl-substituted diacetylenes tend to crystallize into non-polymerizable parallel stack, we have succeeded in preparation of polymerizable stack of diacetylenes substituted by one aromatic ring at least, using the effects of hydrogen bond between aromatic rings of adjacent monomers,[3] bent structure of the methylene on one side of diacetylene moiety,[4] and fluorine substitution onto an aromatic ring or its substituents.[5] Among these effects, methylene's bent-structure provided us the polymerizable stack at high probability. And thus-prepared polydiacetylenes with directly bound aromatic rings were proven to have higher susceptibilities than usual.[6,7]

In addition, in our previous study on ω-(1,3-butadiynyl) substituted 1-alkanols and alkanoic acids, it has been found that those amphiphilic compounds can also be polymerized in solid state though the polymerization scheme was not conventional stereo-regulated 1,4-addition, but 1,4-addition with a small extent of 1,2- or 3,4-additions.[8] It seemed that the solid-state polymerizability and/or the polymerizable stack arises from the packing motif of long-alkyl amphiphilic molecules. It means that those molecules also execute the effect of methylene's bent-structure described above to some extent.

Thus, in the present study,[9] we synthesized ω-(4-aryl-1,3-butadiynyl) substituted alkanols and alkanoic acids and investigated their solid-state polymerization.

Experimental

Synthesis of Monomers. Synthetic process for 27-aryl-24,26-heptacosadiyn-1-ols (**1**) and -diynoic acids (**2**) are summarized in Fig. 1. 24-Pentacosayn-1-ol (**3**), 28-methyl-24,26-nonacosadiyne-1,28-diol (**4**), 24,26-heptacosadiyn-1-ol (**5**), and 24,26-heptacosadiynoic acid (**6**), were synthesized as described in the previous paper.[8] The attached aromatic groups for **1** and **2** were phenyl (**a**), 2-tolyl (**b**), 3-tolyl (**c**), 4-tolyl (**d**), and 9-anthryl (**e**) as usual aromatic hydrocarbons, and pentafluorophenyl (**f**), 2-(trifluoromethyl)phenyl (**g**), 3-(trifluorometyl)phenyl (**h**), 4-(trifluoromethyl)phenyl (**i**), 2,5-bis(trifluoromethyl)phenyl (**j**) and 3,5-bis(trifluoromethyl)phenyl (**k**) as the fluorine substituted aromatic groups. The latter fluorinated groups are the substituents of highly polymerizable symmetrical diacetylenes.[7,10] As donor and/or acceptor substituted aromatic groups, 2-nitrophenyl (**l**), 3-nitrophenyl (**m**), 4-nitrophenyl (**n**), 4-(*N*,*N*-dimethylamino)phenyl (**o**) and 2-amino-5-nitrophenyl (**p**) were also investigated. The formulae of these aromatic substituents are shown in Fig. 2. Details of the synthetic procedures are described below.

27-Phenyl-24,26-heptacosadiyn-1-ol 1a from 3:[11] To a solution of **3** (1.02 g, 2.8 mmol) in the mixture of methanol (5 cm^3) and 2-aminopropane (30 cm^3) with 140 mg of copper(I) chloride, (2-bromoethynyl)benzene (1.52 g, 8.4 mmol) was added dropwise for 2 h at ambient temperature under an argon atmosphere. When the solution became blue upon the addition of (2-bromoethynyl)benzene, a sufficient amount of hydroxylamine hydrochloride was added until the solution became yellow. After finishing addition of (2-bromoethynyl)benzene, the solution was stirred for 2 h and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform) to give 190 mg (15%) of **1a** as colorless crystals.

1a from 5:[12,13] To a solution of **5** (350 mg, 0.9 mmol) and iodobenzene (367 mg, 1.8 mmol) in the mixture of benzene (50 cm^3) and triethylamine (50 cm^3), bis(triphenylphosphine)palladium(II) chloride (15 mg) and copper(I) chloride (1 mg) was added at ambient temperature under an argon atmosphere. After this was stirred for 5 h, the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, chloro-

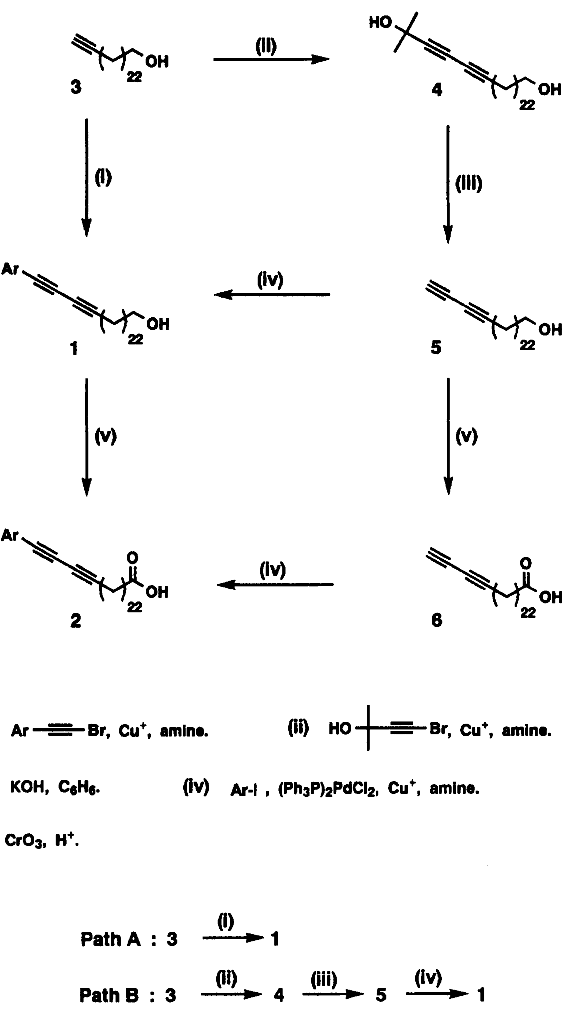

Fig. 1. Synthetic scheme of **1** and **2**.

form) to give 290 mg (69%) of **1a**.

Other alcohol derivatives of **1b**—**1n** and **1p** were also synthesized from **5** and corresponding iodoarene according to the method described above. The yields were as follows; **1b**, 38%; **1c**, 39%; **1d**, 32%; **1e**, 16%; **1f**, 65%; **1g**, 59%; **1h**, 54%; **1i**, 75%; **1j**, 72%; **1k**, 71%; **1l**, 76%; **1m**, 88%; **1n**, 98%; **1p**, 55%.

27-Phenyl-24,26-heptacosadiynoic Acid 2a from 1a:[14] To a solution of **1a** (278 mg, 0.6 mmol) in acetone (200 cm^3), Jones reagent[15] was added dropwise at 0 °C. At first, the color of the solution became dark green. Addition was continued until the color of the solution became greenish orange. Then 2-propanol was added to quench the oxidative activity of 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. Chloroform layer was dried with anhydrous magnesium sulfate and filtered. The solvent in the filtrate was removed under reduced pressure and the residue was purified by column chromatography (silica gel, chloroform) to give 175 mg (61%) of **2a**.

Other carboxylic acid derivatives except **2e**, **2o**, and **2p** were also synthesized by Jones oxidation of corresponding alcohol derivatives according to the method described above. The yields were as follows; **2b**, 33%; **2c**, 30%; **2d**, 83%; **2f**, 69%; **2g**, 58%; **2h**, 60%; **2i**, 52%; **2j**, 54%; **2k**, 56%; **2l**, 22%; **2m**, 54%; **2n**, 47%.

27-(9-Anthryl)-24,26-heptacosadiynoic Acid 2e from 6: To a solution of **6** (302 mg, 0.75 mmol) and 9-iodoanthracene (302 mg, 1 mmol) in the mixture of benzene (50 cm^3) and triethylamine (50 cm^3), bis(triphenylphosphine)palladium(II) chloride (15 mg) and copper (I) chloride (1 mg) was added at ambient temperature under an argon atmosphere. After this was stirred for 5 h, the solvent was removed under reduced pressure. The residue was poured into diluted hydrochloric acid and was extracted with chloroform. The chloroform layer was dried with anhydrous magnesium sulfate and filtered. The solvent of filtrate was removed and the residue was purified by column chromatography (silica gel, chloroform) to give 60 mg (14%) of **2e**.

2o and **2p** were also synthesized from **6** and 4-iodo-*N*,*N*-dimethylaniline or 2-iodo-4-nitroaniline according to the method described above. The yields of **2o** and **2p** were 23 and 42%, respectively.

Table 1 lists up melting points, IR absorption bands of acetylenic moieties, and the results of elemental analysis of synthesized compounds. Chemical structures of each compound were also confirmed by ^{1}H NMR spectra.

Polymerization. In γ-ray induced polymerization, the crystals were sealed in glass tubes under reduced pressure. The dose rate of γ-rays from ^{60}Co was about 0.15 Mrad h^{-1}. Photopolymerization was stimulated by UV irradiation: Samples were irradiated by an 8 W UV lamp (Tokyo Kogaku Kikai K. K., PUV-1A) at a distance of 2 cm. Samples for spectroscopic studies of crystals were KBr-pelletized disks of the diacetylene microcrystals.

Spectroscopy and X-Ray Diffractions. Visible spectra were measured using Shimadzu UV-220 and UV-240. IR spectra were measured using a JASCO IR-810. X-ray diffraction patterns were recorded on a Philips PW-1700 using a Cu $K\alpha$ radiation source.

Results and Discussion

Synthesis of 1. Two methods for synthesis of ω-(4-aryl-1,3-butadiynyl) substituted 1-alkanol **1** were performed. One was a coupling reaction of ω-ethynyl substituted 1-alkanol **3** and (2-bromoethynyl)arene with copper(I) ion as a catalyst in amine (Path A). And the other method was a palladium(0) catalyzed coupling reaction of ω-(1,3-butadiynyl) substituted 1-alkanol **5** and iodoarene in amine. The alcohol **5** was synthesized via **4** from **3**, and **1** could be obtained through the three step reactions (Path B). When **1a**, in which a phenyl group was attached as an aryl group, was synthesized by the two methods, over all yield of Path B (31%) was higher than the yield of Path A (15%). There are some possibilities to increase the yield of Path A by changing reaction conditions such as reaction temperature, solvent and so on. However, from the point of view of the synthesis for ω- (4-aryl-1,3-butadiynyl) substituted alkanols with varieties of aryl groups, Path B had more advantages because easily available iodoarene with many kinds of aryl groups could be used. Then other aryl-substituted derivatives of **1** were synthesized along Path B.

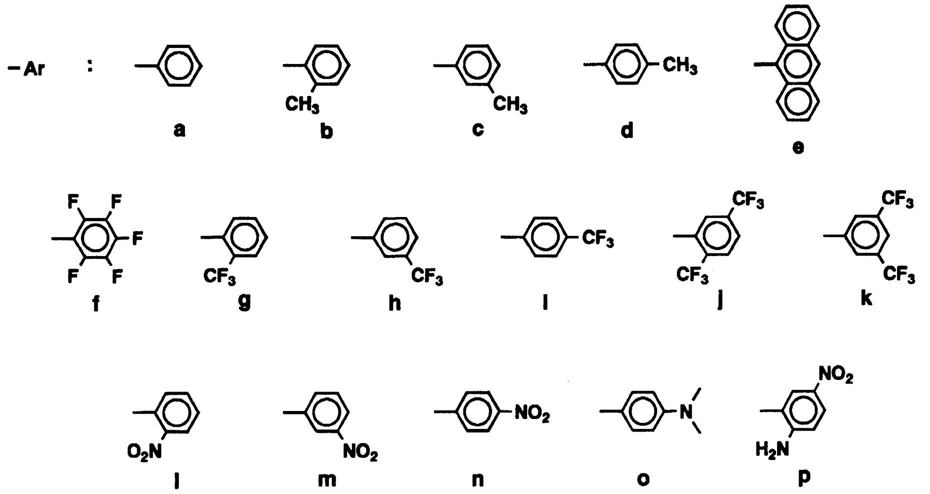

Fig. 2. Formulae of the aromatic substituents for **1** and **2**.

Table 1. ω-(4-Aryl-1,3-butadiynyl) Substituted Alkanols and Alkanoic Acids

Compound	Mp	$\nu_{C\equiv C}$[a)]	Found (Calcd)/%		
	°C	cm^{-1}	C	H	N
1a	80—81	2237	85.35;	11.51	
			(85.28;	11.28)	
1b	67.5—71	2247(w), 2146(vw)	85.59;	11.09	
			(85.29;	11.37)	
1c	66—68	2242, 2151	85.23;	11.47	
			(85.29;	11.37)	
1d	91—93	2247, 2160(w),	84.99;	11.67	
		2152(w)	(85.29;	11.37)	
1e	96.5—98.5	2232(w), 2146(vw)	86.95;	9.93	
			(87.18;	9.99)	
1f	87.5—88	2247	71.70;	8.82	
			(71.45;	8.54)	
1g	74—75.5	2247	76.58;	9.79	
			(76.65;	9.65)	
1h	70—71.5	2247, 2146(w)	76.51;	9.54	
			(76.65;	9.65)	
1i	91—91.5	2247	76.75;	9.52	
			(76.65;	9.65)	
1j	87—88	2247, 2227(sh)	69.75;	8.54	
			(69.97;	8.39)	
1k	81.5—83	2247, 2232(sh)	70.09;	8.34	
			(69.97;	8.39)	
1l	89—92	2237	77.76;	10.17;	2.73
			(77.75;	10.08;	2.75)
1m	98—98.5	2262(sh), 2247,	77.78;	9.89;	2.79
		2155(w)	(77.75;	10.08;	2.75)
1n	104—106	2247	77.74;	10.08;	2.57
			(77.75;	10.08;	2.75)
1p	106—107	2247	75.49;	9.87;	5.12
			(75.53;	9.99;	5.34)

γ-Ray Induced Polymerization. Though 13-phenyl-10,12-tridecadiynoic acid having eight methylenes, i. e. a shorter methylene-chain derivative of **2a**, is reported as a photostable compound,[16)] all crystals of **1** and **2** having more than twenty methylenes became orange or red or blue color by γ-ray irradiation. These color changes show that polymerization or oligomerization occurred more or less for these compounds. Table 2 shows the polymer yields calculated from the weight of the chloroform insoluble part. Though the polymer yield of ω-(1,3-butadiynyl) substituted 1-alkanol, i. e. 22,24-pentacosadiyn-1-ol, reached about 100%,[8)] that of ω-(4-phenyl-1,3-butadiynyl) derivative **1a** was only 2%. Polymer yields of tolyl- and anthryl-substituted

Table 1. Continued

Compound	Mp	$\nu_{C\equiv C}$[a]	Found (Calcd)/%		
	°C	cm^{-1}	C	H	N
2a	92—94	2247, 2255(w)	82.70;	10.33	
			(82.79;	10.53)	
2b	88—90	too weak	82.53;	10.46	
			(82.87;	10.64)	
2c	79—80.5	2247, 2155	83.18;	10.75	
			(82.87;	10.64)	
2d	99.5—100.5	2247(w)	82.67;	10.48	
			(82.87;	10.64)	
2e	91—93	2237(w), 2146(w)	85.35;	9.46	
			(85.07;	9.40)	
2f	102.5—104	2247	69.55;	8.25	
			(69.70;	7.98)	
2g	92—95	2247	74.94;	9.13	
			(74.69;	9.03)	
2h	85—87.5	2252	74.78;	9.01	
			(74.69;	9.03)	
2i	100—102.5	2247	74.42;	9.34	
			(74.69;	9.03)	
2j	104.5—106	2247	68.20;	8.02	
			(68.38;	7.87)	
2k	91.5—93.5	2247, 2237(sh)	68.39;	7.70	
			(68.38;	7.87)	
2l	108.5—110	2247(w)	75.77;	9.39;	2.57
			(75.68;	9.43;	2.67)
2m	102—103	2262(sh), 2247	75.78;	9.45;	2.60
			(75.68;	9.43;	2.67)
2n	111—112.5	2247	75.49;	9.34;	2.85
			(75.68;	9.43;	2.67)
2o	104—106	2242, 2141	80.39;	10.81;	2.62
			(80.56;	10.62;	2.68)
2p	118—119.5	2247, 2151	73.79;	9.45;	5.04
			(73.57;	9.35;	5.20)

a) KBr-pelletized sample; (w): weak, (vw): very weak, (sh): shoulder.

Table 2. Solid-State Polymerizabilities of **1** and **2** upon γ-Ray Irradiation

Aromatic substituents	Polymer yield / % (γ-ray dose / Mrad)	
	1	**2**
a	2 (20)	27 (20)
b	1> (100)	53 (100)
c	7 (100)	6 (100)
d	1> (100)	50 (100)
e	1> (100)	6 (100)
f	82 (20)	47 (53)
g	11 (100)	1 (53)
h	1> (100)	36 (53)
i	18 (100)	89 (50)
j	98 (50)	97 (30)
k	1> (50)	6 (31)
l	1> (100)	1> (53)
m	1 (100)	21 (53)
n	11 (50)	73 (30)
o		72 (100)
p	3 (100)	20 (100)

ones **1b**—**1e** were also low yield of less than 7%. However, that of pentafluorophenyl derivative **1f** rose up to 82%. In the case of (trifluoromethyl)phenyl derivatives, polymer yields were higher than those of corresponding tolyl derivatives except those substituted at the 3-position. 2,5-Bis(trifluorometyl)phenyl subtituted derivative **1j** polymerized in almost quantitative yield. The tendency that fluorinated 1,4-diphenyl-1, 3-butadiynes, such as 1,4-bis(2,5-bis(trifluoromethyl)-phenyl)-1,3-butadiyne (DFMP), 1,4-bis(4-butyl-2,3,5, 6-tetrafluorophenyl)-1,3-butadiyne (BTFP) and so on, show higher polymerizability than the corresponding non-fluorinated ones have already been reported.[10] The reason, why the fluorinated phenyl diacetylenes are so often highly polymerizable, is not clear at present since the crystal structures of monomers have not been determined due to their high polymerizability by X-ray even at liquid nitrogen temperature. However, the polymer crystal structures obtained from three 1,3-butadiynes substituted by one or two fluorinated-phenyl groups, i.e. DFMP, BTFP, and 1-(3-(methylamino)phenyl)-4-(3,5-bis(trifluorometyl)phenyl)-1,3-butadiyne (MADF), have been analyzed and their 1,4-addition polydicacetylene structures were confirmed.[5,7] Strong local dipoles of C–F bonds may disturb simple parallel stack and therefore provide almost half-a-molecule-displaced polymerizable stack. Comparatively weak intermolecular interaction between fluorinated monomers may facilitate molecular motions necessary for the polymerization reaction.

The polymer yields of carboxylic acid derivatives were higher than those of the corresponding alcohol derivatives in most cases. These were opposite results to the case of ω-butadiynyl derivatives, i. e. ω-butadiynyl substituted alkanols were more polymerizable than the corresponding alkanoic acids.[8] Since single crystals of these derivatives with a long methylene chain were hard to obtain and X-ray crystal structure analyses were impossible, we estimated this polymerzability difference from the difference in molecular structures as follows. This could be considered from the combination of the bulkiness of the compounds' both ends. In the hydrophilic ends, the volume of the carboxylic group is larger than that of the hydroxymethyl group, whereas in the hydrophobic ends, the volume of aryl groups in ω-arylbutadiynyl dervatives are larger than that of the hydrogen in ω-butadiynyl derivaitves. From the point of view of these classification, in the case of the large volume combination or the small volume combination in both ends, i. e. ω-(4-aryl-1,3-butadiynyl) substituted alkanoic acids or ω-butadiynyl substituted alkanols, the polymerizabilities became higher. On the other hand, in the case of the combination of the large and small substituents, the polymerizabilities became lower. These results suggested that the closer the relative volume of the hydrophilic and the hydrophobic ends, the packing of methylene chains became more tight to make highly polymerizable arrangement of diacetylene moieties. Proper balance of the substitutent bulkiness of both ends are necessary to realize the well-polymerizable stack.

This fact was also confirmed by the crystallinity of polymers. As a typical example, powder X-ray diffraction patterns of monomers and polymers of **1j** and **2j**, which were 2,5-bis(trifluoromethyl)phenyl substituted dervatives and both monomers showed higher polymerizabilities, were measured. Both monomers showed the main diffraction peaks around 19—20° in 2θ angles, corresponding to the spacing of the methylene chain packing of about 0.44—0.47 nm. In the case of the carboxylic acid derivative of **2j**, the crystallinity was not so reduced after polymerization. However, in the case of the alcohol derivative of **1j**, diffraction intensity of its polymer decreased to less than about one seventh of that of the monomer. This result indicates the following things. The carboxylic acid derivatives aligned in more favorable stack to polymerize in crystals and were polymerized maintaining the crystallinity. On the other hand, in the alcohols, the crystallinity was lost more or less during polymerization.

Photopolymerization. In order to study the relation between the polymerizability and the absorption, visible absorption spectral changes of the KBr-pelletized samples of the monomers during UV-irradiation were investigated. Typical absorption change was shown in Figs. 3 and 4. Absorption spectra of polymers could be roughly classified into the following three groups. The first one shows absorption increase in the shorter-wavelength region than absorption edge without the appearance of new absorption maxima in visible region, e. g. the spectral change of **1a** as shown in Fig. 3-(a). This spectrum resembles to that of ω-butadiynyl substituted alkanols.[8] The second one has absorption maxima which can be observed as characteristics of conventional polydiacetylenes, e. g. the spectral change of **1f** as shown in Fig. 3(b). Hereafter these two types of compounds are called Type 1 and Type 2, respectively. The third one is for the absorption except Types 1 and 2, and was further divided into the three groups, i. e. Types 3—5. The compound in Type 3 showed the intermediate absorption between Types 1 and 2, e. g. the spectral change of **2f** as shown in Fig. 4(a). The compounds with 2,5-bis(trifluorometyl)phenyl (**1j** and **2j**) and 2-nitrophenyl (**1l** and **2l**) groups showed spectra peculiar to their substituents, and they were classified to Types 4 and 5, respectively. Figure 4(b) and (c) show the spectral changes of **1j** and **2l** as examples of Types 4 and 5. Table 3 summarizes classification of the absorption spectra during polymerization for all the compounds.

The compounds in Type 1 generally showed rather low polymer yield of less than about 20% even after γ-ray irradiation of 50—100 Mrad though the yield of

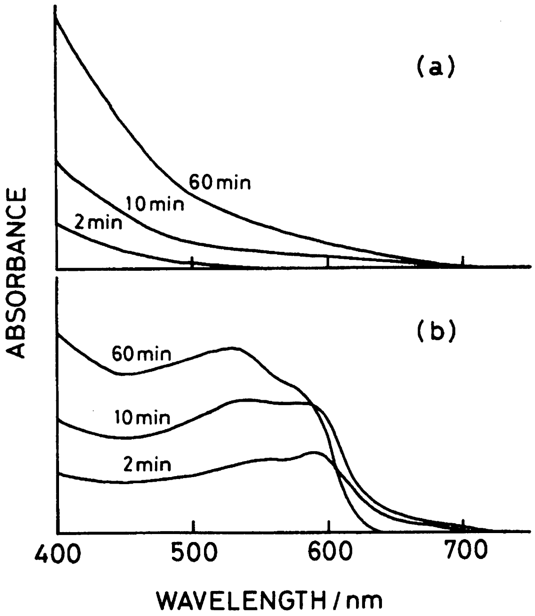

Fig. 3. Visible spectral change of **1a** ((a): Type 1) and **1f** ((b): Type 2) depending on UV irradiation time.

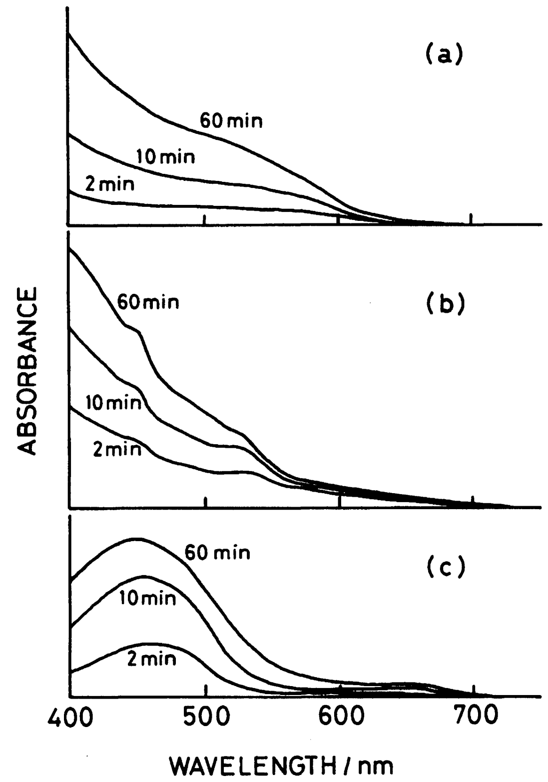

Fig. 4. Visible spectral change of **2f** ((a): Type 3), **2j** ((b): Type 4) and **2l** ((c): Type 5) depending on UV irradiation time.

Table 3. Classification of Visible Absorption Spectral Change during UV Irradiation

Aromatic substituents	Type of spectrum	
	1	2
a	Type 1	Type 1
b	Type 1	Type 2
c	Type 1	Type 2
d	Type 1	Type 2
e	Type 1	Type 1
f	Type 2	Type 3
g	Type 1	Type 1
h	Type 3	Type 3
i	Type 3	Type 2
j	Type 4	Type 4
k	Type 2	Type 2
l	Type 5	Type 5
m	Type 1	Type 1
n	Type 3	Type 2
o		Type 2
p	Type 1	Type 1

the compound **2a** was 27% by 20 Mrad dose as an exception. Since ω-butadiynyl substituted alkanols which showed similar spectral change during polymerization were found to be polymerized without regularity of 1,4-addition,[8] the compounds in Type 1 are probably polymerized in the same manner and effective conjugation length of the polymer backbone is not extended.

On the other hand, the compounds in Type 2 showed higher polymer yields more than 50% with the exceptions of **1c**, **1k**, and **2k**. And characteristic absorption peaks of polydiacetylenes clearly indicates that polymerization of the compound in Type 2 proceeded by topochemical 1,4-addition. The longest wavelength of the absorption maxima of this series were observed around 680 nm in **2o**. That wavelength is one of the longest ones for polydiacetylenes with aromatic substituents directly bound to the main chain, e. g. the polymers from 5-(*N*-carbazolyl)-2,4-pentadiyn-1-ol (CPDO) showed absorption maximum at 670 nm.[4] Since electron-donating aromatic groups were attached directly to the main chain in the compound **2o** and CPDO, i. e. 4-(*N*,*N*-dimethylamino)phenyl group for **2o** and *N*-carbazolyl group for CPDO, introduction of electron-donating group as a substituent of polydiacetylene seems to be effective to shift the absorption maximum to longer wavelength.

The compounds in Type 3 showed intermediate polymerizability between Types 1 and 2, and their polymer yields varied from 1 to 50%. Thus, it seemed that the qualitative order of the polymerizability of this series of compounds was Type 2, Type 3, and Type 1, according to the intensity of excitonic absorption appeared during polymerization with the exception of the following two types.

Though 2,5-bis(trifluoromethyl)phenyl derivatives included in Type 4 showed unique undulate absorption spectra without clear excitonic bands, their polymer yields were very high. In the case of 2-nitrophenyl derivatives classified to Type 5, absorption maximum was observed around 460 nm. This maximum wavelength is blue-shifted compared with that of conventional polydiacetylenes. Since the polymer yields of these derivatives were very low, it is clear that absorption around 460 nm is not based on excitonic ones which appears in conventional polydiacetylenes.

In conclusion the amphiphilic diacetylenes with directly-bound aromatic substituents were synthesized and it was found that the effect of the packing of the methylene chains makes those derivatives aligned in the solid-state polymerizable stack. The difference of polymerizabilities between the alcohols and the carboxylic acids was estimated from the relationship of the bulkiness of two molecular ends. Fabricatability of monolayers and multilayers, and polymerization behavior in multilayers of this series of compounds were reported in a separated paper.[17]

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