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PREPARATION AND NONLINEAR OPTICAL PROPERTY OF POLYDIACETYLENES FROM UNSYMMETRICAL DIPHENYLBUTADIYNES WITH TRIFLUOROMETHYL SUBSTITUENTS

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Abstract In order to obtain the polydiacetylenes having π-conjugation between polymer backbone and side chains, many of unsymmetrical diphenylbutadiyne derivatives with trifluoromethyl substituents on one of the phenyl rings have been synthesized. Among them, 1-(3-(methylamino)phenyl)-4-(3,5-bis(trifluoromethyl)-phenyl)butadiyne (MADF) was found to be topochemically polymerized with complete conversion into the polymer single crystals. Spectroscopies and X-ray crystal structure analysis revealed that the π-conjugation of this polymer are more extended than those of the so-far prepared poly(diphenylbutadiyne)s, with smaller dihedral angles between π-conjugation planes of polymer backbone and phenyl rings. The extended π-conjugation was also confirmed by larger $\chi^{(3)}$ values.

INTRODUCTION

Polydiacetylenes, which can be obtained as peculiar single crystals of conjugated polymers by solid-state polymerization, have attracted much attention for their large third order nonlinear optical susceptibilities.[1,2] In order to improve them further more, polydiacetylenes having π-conjugation between polymer backbone and side chains, namely, those with aromatic rings directly bound to the main chain and therefore enlarged polarizability must be better candidates. However only a few polymerizable diphenylbutadiyne derivatives, e.g., bis(3-acetylamino-phenyl)butadiyne (m-AAPB),[3] bis(4-butyl-2,3,5,6-tetra-fluorophenyl)butadiyne (BTFP)[4] and bis(2,5-bis(trifluoro-

methyl)phenyl)butadiyne (DFMP),[4] were known. Previously, we analyzed the crystal structure of m-AAPB, and clarified that hydrogen bonds between amide groups of adjacent phenyl rings are effective to form a polymerizable packing.[5] By utilizing the hydrogen bond effect for the design and synthesis of unsymmetrical diphenylbutadiynes, we could obtain many polymerizable crystals, such as 1-(3-nitrophenyl)-4-(3-(octadecanoylamino)phenyl)butadiyne, N,N'-bis-(3-((3-nitrophenyl)butadiynyl)phenyl)eicosadiamide and so on.[6,7]

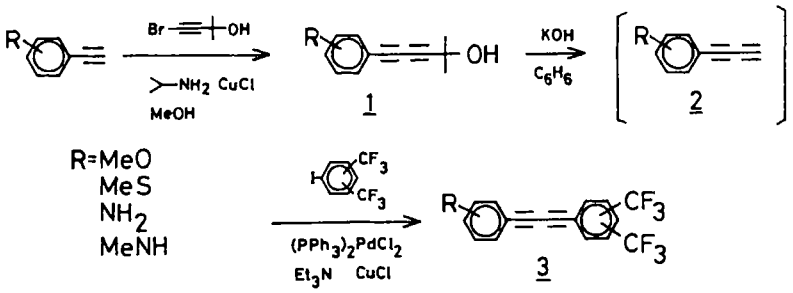
Fluorine containing phenyl groups also seem to be effective to form a polymerizable stack.[4] Therefore, in the present study, 2,5- and 3,5-bis(trifluoromethyl)phenyl groups were selected as one of the two substituents of butadiyne. As the other substituent electron-donating phenyl groups were selected so as to enlarge the polarizability of the diphenylbutadiyne moiety. Thus many of new unsymmetrical diacetylenes have been synthesized and their solid-state polymerizabilities have been investigated together with the structure and the nonlinear optical property of the representative polymer.

EXPERIMENTAL SECTION

Synthesis

Unsymmetrical diphenylbutadiyne derivatives 3 were synthesized according to the procedures shown in SCHEME 1. Experimental details are as follows.

Synthesis of Arylhexadiynols 1; General Procedure: Cuprous chloride (0.1g, 1mmol) was dissolved in isopropylamine (20ml) and methanol (10ml) under an argon atmosphere. Ethynylarene (10mmol) was added to the solution and then 4-bromo-2-methyl-3-butyn-2-ol (1.95g, 12mmol) was added over 1h. When the solution became blue due to the presence of the cupric ion, a little amount of hydroxylamine hydrochloride was added for reduction of cupric ion to form cuprous ion. After stirring for an additional 3h the mixture was extracted with benzene (50ml×3) and dried with anhydrous magnesium sulfate. The



SCHEME 1

solution was filtered and the solvent was removed. The crude product was purified by column chromatography on silica gel using benzene as eluent. Removal of solvent provides products of 1, and their chemical structures were confirmed by IR and ^{1}H-NMR spectroscopies.

Synthesis of Diarylbutadiynes 3; General Procedure: 1 (5mmol) was dissolved in benzene (100ml), and powdered potassium hydroxide (0.028g, 0.5mmol) was added. The mixture was stirred under reflux for 15min. The crude product was chromatographed on silica gel using benzene as eluent, and the solution was concentrated. The resulting solution of arylbutadiyne 2 was added to the mixture of bis(trifluoromethyl)iodobenzene (5mmol), bis(triphenylphosphine)palladium(II) chloride (0.35g, 0.5mmol) and cuprous chloride (0.1g, 1mmol) in triethylamine (50ml), and stirred for 5-12h under an argon atmosphere. The mixture was extracted with ether (50ml×3). The ether solution was washed with water, and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent was removed. The crude product was purified by column chromatography on silica gel using benzene-hexane mixture as eluent. Removal of solvent provides products of 3, which was recrystallized from an appropriate solvent. The data of compounds 3 were as follows:

3b: Over all yield 20%; m.p. 37°C (hexane); IR(KBr) 2845, 2225, 1600, 1430, 1140 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ=3.81(3H, s), 6.96(1H, dd, J=8.2, 2.5Hz), 7.06(1H, d, 2.5Hz), 7.15(1H, d, J=7.6Hz), 7.26(1H, dd, J=8.2, 7.6Hz), 7.68(1H,

d, J=8.3Hz), 7.80(1H, d, J=8.3Hz), 7.92(1H, s). Found: C, 61.63; H, 2.96%. Calcd for $C_{19}H_{10}OF_6$: C, 61.97; H, 2.74%.

3c: Over all yield 46%; m.p. 86-88°C (ethanol); IR(KBr) 2850, 2220, 1605, 1425, 1140 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ=3.84(3H, s), 6.88(2H, d, J=8.8Hz), 7.51(2H, d, J=8.8Hz), 7.68(1H, d, J=8.3Hz), 7.80(1H, d, J=8.3Hz), 7.92(1H, s). Found: C, 61.65; H, 2.86%. Calcd for $C_{19}H_{10}OF_6$: C, 61.97; H, 2.74%.

3s: Over all yield 45%; m.p. 75-76°C (ethanol); IR(KBr) 3330, 2830, 1605, 1295, 1130 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ=2.84(3H, s), 3.80(1H, broad s), 6.65(1H, dd, J=8.2, 2.4Hz), 6.75(1H, d, J=2.4Hz), 6.90(1H, d, J=7.6Hz), 7.15(1H, dd, J=8.2, 7.6Hz), 7.83(1H, s), 7.93(2H, s); ^{13}C-NMR($CDCl_3$) δ=30.2, 71.8, 77.3, 77.4, 84.5, 114.5, 115.3, 121.2, 121.5, 122.0(qq, $^3J_{C-F}$=4, 4Hz), 122.6(q, $^1J_{C-F}$=273Hz), 124.4, 129.1, 131.9(q, $^2J_{C-F}$=34Hz), 132.0(q, $^3J_{C-F}$=3Hz), 149.2. Found: C, 62.21; H, 3.21; N, 3.99%. Calcd for $C_{19}H_{11}NF_6$: C, 62.13; H, 3.02; N, 3.81%.

Chemical structures of other compounds were also confirmed by IR and ^{1}H-NMR spectroscopies and melting points of 3 are shown in TABLE I.

Solid-State Polymerization

Polymerizability check of the crystals was carried out by γ-ray or UV irradiation at room temperature. γ-ray source of ^{60}Co with the dose rate of 1Mrad/h or a low-pressure mercury lamp (8W) was used for the polymerization. Polymer conversion was determined by relative intensities of two IR absorption bands, i.e., stretching bands corresponding to carbon-carbon triple bonds and aromatic rings. Graviometry after extraction of monomer was also used for confirmation of conversion.

X-ray Crystallography

X-ray powder diffraction patterns were recorded on a Philips PW-1700 diffractmeter by using the CuKα line (λ=1.542A). Polymer single crystal of 3s for X-ray crystal structure analysis was obtained by following procedures;

TABLE I Solid-state polymerizability and melting points of 3.

-R	2,5-CF_3			3,5-CF_3		
	No.	m.p.(°C)		No.	m.p.(°C)	
2-MeO	3a	86-87	-	3k	93-94	-
3-MeO	3b	37	+	3l	47-48	-
4-MeO	3c	86-88	+	3m	88-89	-
4-MeS	3d	101-103	-	3n	83-84	-
2-NH_2	3e	91	-	3o	112	-
3-NH_2	3f	86-87	-	3p	64	-
4-NH_2	3g	117-118	-	3q	93-94	-
2-MeNH	3h	107-108	-	3r	70-71	-
3-MeNH	3i	70-71	-	3s	75-76	+
4-MeNH	3j	98-99	-	3t	51	-

+ polymerizable - stable

Monomer single crystal was grown by slow evaporation of ethanol solution. After cutting the crystal into proper size for X-ray crystallography, it was subjected to γ-ray polymerization to give polymer single crystal. Cell parameters and full intensity data were derived from the measurements on a NONIUS 4-circle diffractometer (CAD4SDP MicroVAXII) at room temperature. The structure was determined and refined by use of SHELX 76.

Evaluation of Third Order Nonlinear Optical Susceptibility $\chi^{(3)}$

The $\chi^{(3)}$s of third harmonic generation (THG) were evaluated by Maker fringe method.[8] Samples were prepared as follows. Thin films of monomers were first prepared by physical vapor deposition or by recrystallization from molten state between two quartz plates, and were polymerized as was described above.

Spectroscopy

IR and visible absorption spectra were measured by a JASCO IR-810 and a Shimadzu UV-220, respectively. Absorption changes during polymerization were followed with KBr-

pelletized specimens of the compounds. NMR spectra were measured by a Nicolet NT-360 and a JEOL JNM-GSX270.

RESULTS AND DISCUSSION

The solid-state polymerizabilities of 3 upon UV-irradiation are listed in TABLE I. Since several of symmetrical diphenylbutadiynes with fluorine substitution are known to be polymerizable, we expected that unsymmetrical butadiyne derivatives having the same type of fluorine substitution on one side of phenyl rings would be polymerizable. However, among twenty compounds prepared, only three, i.e., 3b, 3c and 3s were polymerizable. In other words, the majority of 3 crystallize in photostable packing. One of the reasons for such stability may be the enlarged polarization in the present molecules. In our previous study to prepare polydiacetylenes with one aromatic substituent directly bound to the polymer backbone, we demonstrated that the bending effect, i.e., a kind of a steric effect works with a high probability to form a polymerizable stack.[9,10] From the present study it seems that the delicate balance of steric and electrostatic effects would be important to attain a polymerizable stack if the molecules have not the bending effect but large dipoles.

Visible absorption spectral changes of 3s during UV-irradiation are shown in FIGURE 1. The absorption maxima of polymer are observed at 640, 590 and 550nm. Other two compounds also became deeply blue-colored polymers with metallic lusters. From those color changes, it is obvious that the polymerization proceeds by 1,4-addition, the same manner as those of conventional diacetylenes. Polymer conversions upon γ-ray irradiation are shown in TABLE II. In the case of 3c, polymerization proceeded much slowly and X-ray powder diffraction patterns of the polymer became broad, indicating that the crystalline lattice was deteriorated in the course of polymerization. On the other hand, 3s (MADF) showed higher polymer conversion of 90%, and the polymer single crystal was obtained by a single-

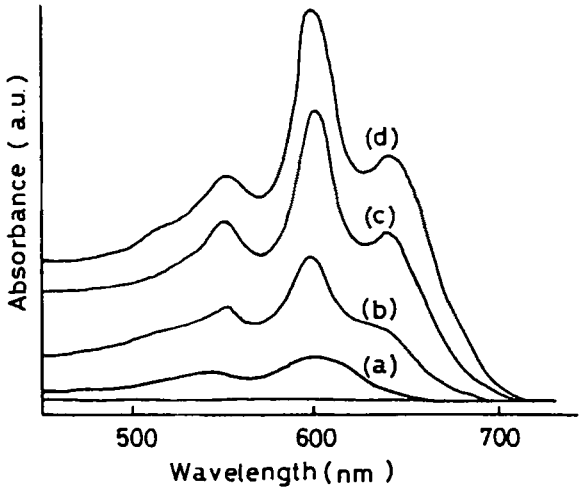


FIGURE 1 Absorption spectra of 3s dispersed in potassium bromide after 1min (a), 5min (b), 22min (c) and 45min (d) of UV-irradiation.

TABLE II Polymer conversions of 3c and 3s upon γ-ray irradiation.

No.	γ-ray dose (Mrad)	Polymer conversion (%) (a)	(b)
3c	320	45	40
3s	130	70	72
	240	91	90

(a) Calculated from the weight of benzene insoluble part.

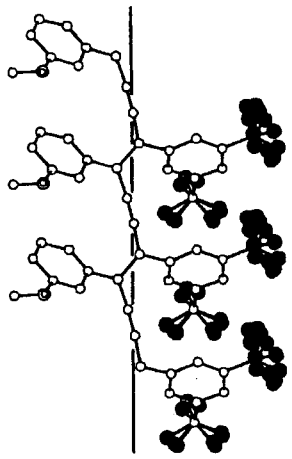
(b) Calculated from relative intensity of $\nu_{C\equiv C}$.

crystal-to-single-crystal polymerization. TABLE III shows the crystallographic data of poly-MADF. In the structure determination fluorine atoms of trifluoromethyl groups were not fixed because of disordering. Consequently, twelve of fluorine atoms were introduced. Full details of the molecular and crystal structures will be published elsewhere. The molecular structure of poly-MADF is shown in FIGURE 2. The dihedral angles between π-conjugation planes of polymer backbone and phenyl rings are 44° for methylaminophenyl ring, and 56° for bis(trifluoromethyl)phenyl ring, respectively. Both of them are smaller

than those of previously studied symmetrical poly(diphenylbutadiyne)s, i.e., 58° for poly-BTFP and 67° for poly-DFMP.[8] It seems that the small dihedral angles of

TABLE III Crystallographic data of poly-MADF.

Formular	$C_{19}H_{11}NF_6$
Mr	367.3
Crystal System	Monoclinic
Space group	$P2_1/a$
a (A)	23.906(5)
b (A)	4.905(1)
c (A)	14.833(3)
β (°)	106.17(2)
V (A^3)	1670(9)
Z	4
Dx(Mg m^{-3})	1.46
Dm(Mg m^{-3})	1.46



○: C , ●: F , ◎: N .

FIGURE 2 The molecular structure of poly-MADF.

the poly-MADF are attained because of only small substituents of hydrogen at the ortho positions of phenyl rings, resulting in that poly-MADF has more extended π-conjugation system. Actually the absorption maximum observed is at 640nm, and is longer than those of symmetrical poly(diphenylbutadiyne)s, i.e., 615nm for poly-BTFP and 560nm for poly-DFMP.

Large third order nonlinear optical properties are expected for poly-MADF because of its smaller band gap estimated from absorption maximum at longer wavelength.[11] So, $\chi^{(3)}$s of THG of this polymer was evaluated. As references, $\chi^{(3)}$s of three known compounds, i.e., poly-PTS, poly-BTFP and poly-DFMP in thin films, were also evaluated under the same experimental conditions. Among these polymers only poly-PTS does not have π-conjugation between polymer backbone and substituents. In the case of the poly-MADF thin films, the polymer crystallites were almost

uniaxially oriented within the area of focused laser. So the THG and/or $\chi^{(3)}$ along the polymer main chain was directly obtained by the measurements using the polarized laser light. In the case of other polymer films, however, polymer crystallites were smaller and were oriented randomly within the laser focusing area. Therefore, the $\chi^{(3)}$ along the polymer chains of these polymer films were derived by multiplying measured data with the correction factor of $(1/\langle\cos^4\theta\rangle)=8/3$. $\chi^{(3)}$s thus obtained are shown in TABLE IV. It is seen that the $\chi^{(3)}$ of poly-MADF in the non-resonant region at the pumping wavelength of 2.16μm is larger than that of poly-BTFP, i.e., the so-far known largest $\chi^{(3)}$ for polydiacetylenes. This must be because of extended π-conjugation between polymer backbone and substituents.

In conclusion, many of unsymmetrical diphenylbutadiyne derivatives with trifluoromethyl group have been synthesized. Among them, MADF can be topochemically polymerized with complete conversion to give the polymer single crystal. The π-conjugation of this polymer are more

TABLE IV $\chi^{(3)}$ values[a] of polydiacetylene thin films.

poly-DA	$\chi^{(3)} \times 10^{11}$ (esu)		
	Pumping wavelength (μm)		
	1.96	2.10	2.16
poly-DFMP[b]		4.5	
poly-BTFP[b]	25	18	11
poly-MADF[c]	30	23	23
poly-PTS[c]		4.0	

[a]These $\chi^{(3)}$ values are for along the main chain direction.

[b]Prepared by physical vapor deposition.

[c]Prepared by recrystallization from molten state between two quartz plates.

extended with the small dihedral angles between π-conjugation planes of polymer backbone and phenyl rings than those of so-far known polydiacetylenes, and the largest $\chi^{(3)}$ for polydiacetylenes has been demonstrated. From the point of view of crystal engineering to design polymerizable diacetylenes, the crystal forming motif of MADF monomer is interesting. The crystal structure analysis is currently in progress.

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